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CORROSION RESISTANCE OF METALS AND ALLOYS

BY
ROBERT J. McKAY
AND
ROBERT WORTHINGTON



American Chemical Society
Monograph Series

Third Printing, 1946

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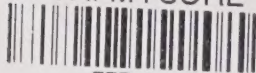
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Corrosion resist.

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company (Reinhold Publishing Corporation, successors) of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is diffi-

cult for any individual to keep in touch with the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's *Handbuch der Organischen Chemie*, Richter's *Lexikon*, Ostwald's *Lehrbuch der Allgemeinen Chemie*, Abegg's and Gmelin-Kraut's *Handbuch der Anorganischen Chemie* and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coordinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coordinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfillment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well-digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large

part upon the measure of cooperation which can be secured in the preparation of books dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

AMERICAN CHEMICAL SOCIETY

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OLD MAN CORROSION

Preface

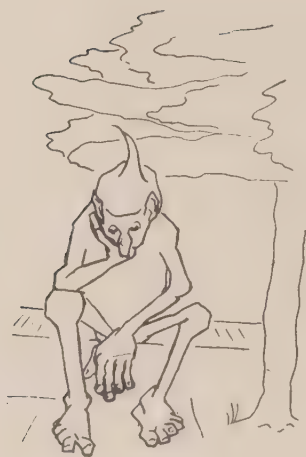
The purpose of this work is to summarize the facts on corrosion processes and rates. It is inevitable that statements on the facts of corrosion rates will find some disagreement on the part of manufacturers and possible users who hope for better resistance properties. It is, of course, often possible to soften bald statements of such a necessarily unpleasant and negative action as the corrosion of a metal, but we feel that a more useful purpose is served by as fair a statement of actual facts as can be given. We hope that critics will realize that this has been our attempt even in those cases where our presentation does not agree with what they would like to see.

The data given mostly cover the facts only; they offer no panacea for corrosion difficulties. In the present state of knowledge of non-ferrous alloy corrosion, it is not possible to give any general methods of prevention. The cure in the majority of cases is to use the right alloy in the right place. Several cases in which definite improvements have been obtained by modification of metals and solutions are indicated under their proper headings, but these cures are hardly general enough to deserve a section of their own. For instance, right at present in such an important case as general corrosion by sea water, we cannot rely fully on the corrosion resistance of any metal but fall back on non-metallic protective coatings rather generally.

We are much indebted to the metal industries of the United States for useful data which have been furnished us from their publications and files. This indebtedness extends to manufacturers of all the metals listed. We hope that the presentation of these data will lead to a sounder and broader use of each metal. We are particularly indebted to the International Nickel Company, Inc., to its President and Executives for their generous forgiveness when the preparation of this work has interfered with our duties, and to the technical staff for assistance on many features.

ROBERT J. MCKAY
ROBERT WORTHINGTON

January 1, 1936.



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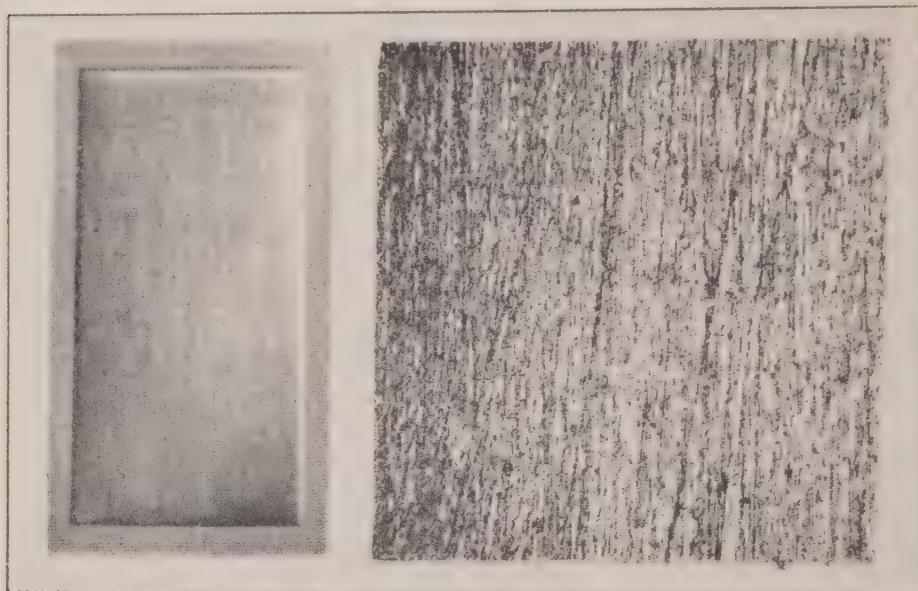
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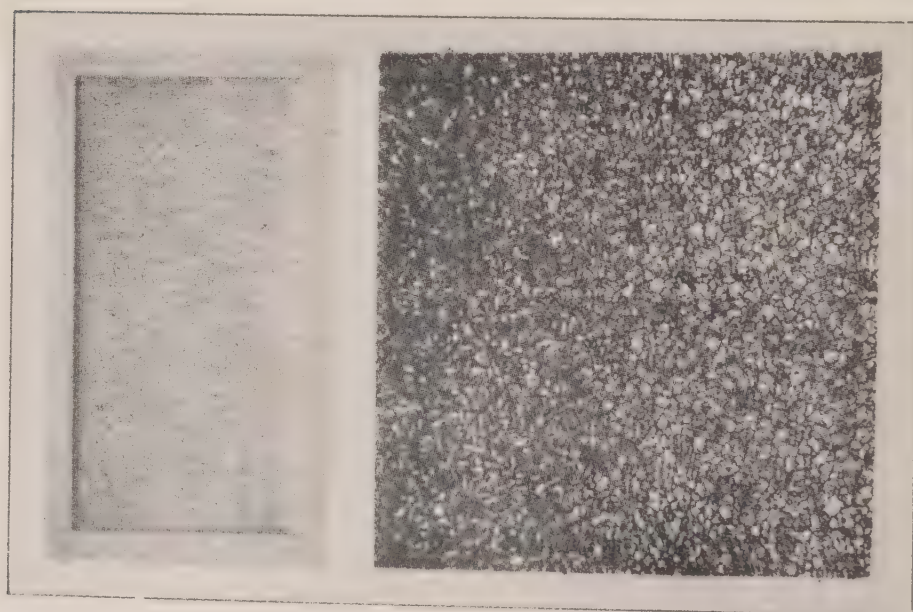
PART I
General and Theoretical



Natural Size

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Sheet with ground finish before corrosion.



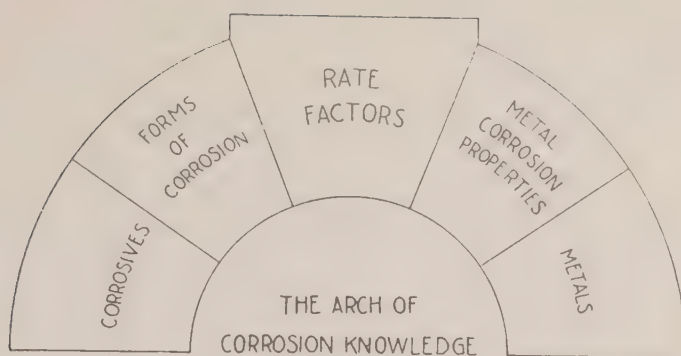
Natural Size

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As directly attacked by the acid.

DIRECT CHEMICAL CORROSION

When strong acid attacks a uniform surface and no films develop the surface corrodes or etches to a regular but somewhat roughened surface



CORROSION RESISTANCE of METALS AND ALLOYS

Introductory

A knowledge of the corrosion resistance of alloys should help to prevent corrosion by indicating the proper use of the right alloy. Data from experience and test on the action of alloys, under given conditions, form the main or second part of this book. This preliminary part attempts to classify and explain the economically important points of the theory or mechanism. Combination of data from Part II with the general facts of Part I should enable the reader to reason for himself on corrosion problems on which direct data are not available.

In this preliminary or theoretical discussion of corrosion we attempt to use the theory concept in a somewhat limited sense (The idea expressed by "theoretical" and its relation to "practical" is a study in itself). If by "theory" we mean a study of how things work as a sound link between cause and effect, then it is a very "practical" study. The development of chemical and general scientific theory, in the last decade or so, has been so rapid that consideration of the theory of things often takes us into concepts that are almost abstract or at least so highly mathematical that some time is required for even the clearest minds to grasp them. On the other hand, without going into abstruse theories, we think it is possible to describe the



DEZINCIFICATION TYPE CORROSION

View of end and section, right, of corroded rod after 18 months service. The removal of one constituent of the alloy while the other stays almost in position has caused only small effect on the surface; while the body of the metal, except for a small core, has lost its strength and ductility.

way corrosion works based on the simpler and more generally understood concepts which have come to be regarded now as "facts" instead of "theories." This method is followed herein with the belief that it furnishes a real guide to procedure in fighting corrosion.

To illustrate the method we may consider the explanation of the theory or mechanism of a sled sliding down an icy incline. The motion is caused by the pull of gravity which is great enough to overcome the friction between sled runners and the icy surface. The speed is affected by the weight of the sled and load, the angle of incline, the frictional properties of runners and surface, the dimensions of runners, etc. The major things which affect the speed can be explained and classified without going into the theory of gravity and acceleration, the theory of stresses on an inclined plane, the theory of friction, and of ice crystallization, although all of these enter into the problem. The motion is understood better by simply accepting and applying the known theories. Such an explanation will, of course, not be satisfactory to one who does not accept, for instance, the same theory of friction as the writer.

The engineer or industrial chemist who has the problem of making a machine or structure last as long as possible in corrosive conditions, should have a general knowledge of how corrosion works but the following of the various theories involved to their ultimate end may interfere with his practical decisions.

Thus in explaining and classifying corrosion, we will not delve into the theories of electrochemistry, of acid-metal reactions, of oxidation, of diffusion, or of metal structure, although it is recognized that each of these has its bearing on the subject. We will assume certain accepted theories as true and we will be subject to the skepticism of those who do not accept them.

In order to present the facts of corrosion in an orderly manner some classification is necessary. Several different methods are satisfactory. We may use, for instance, a classification based on the *corroding conditions*, such as: air, acids, natural waters, etc. There are certain more or less visible or determinable *forms of corrosion* which are typical of certain cases of corrosion and not of others, such as: galvanic action, dezincification, pitting, etc. These may be used as a basis for classification. The rate of corrosion has been found to be affected or controlled by certain *rate factors*, such as: temperature, acidity, electrolytic effects, etc., which are present in most cases, and corrosion may be classified according to these. Then metals have certain *properties* of direct importance in corrosion, such as: solution pressure, work straining, etc., and corrosion may be classified according to these. Lastly, the *metals* which are corroded serve as a very practical

basis for the presentation of data. This is the method used in the presentation of the corrosion data in Part II, where data are grouped under: copper alloys, lead and lead coatings, etc.

In order to clarify these things the various classifications of the parts of the corrosion problem are tabulated opposite. This is done in order, following from (1) properties of the corrosives which cause corrosion through (2) forms which this corrosion takes, to (3) things which affect the rate, to (4) general properties of the metals themselves which affect their corrosion, and giving finally (5) the specific corrosion resistance of the metals. This gives us an outline for the subject which will be found to include the several items which enter into the problem, presenting them so that their relation to each other is roughly indicated. This method produces the following lists of: (1) *corrosives*, (2) *forms of corrosion*, (3) *rate factors*, (4) *metal properties*, and (5) *metals*. See Figure 1.

In these classifications, there are some cases of overlapping and surface inconsistency. For instance, in division 2, one may reasonably believe that all cases of "pitting" are due to "galvanic action" or to "concentration cells," or in line 3, that "films" are formed by "oxidizing agents." A complete explanation of the different shades of meaning resulting in such inconsistencies is not considered necessary because if they are accepted in good faith, it will be seen that they form a useful framework under which each of the subjects listed can be logically described from the standpoint of its relation to corrosion.

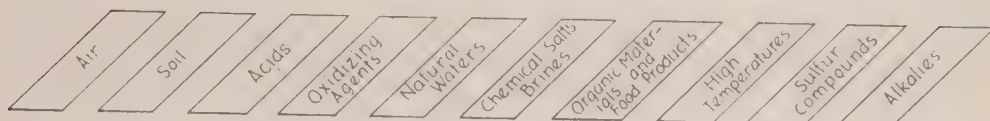
Another roughness in these classifications comes from the fact that some important concepts as acids, oxidizing agents, films, and electrolytic effects, must appear more than once as they are considered from different angles. This may entail some repetition of thought but we believe that this repetition where it occurs is excusable because, after all, such subjects are so important a part of the corrosion mechanism that they cannot be emphasized too much nor understood too well.

The general form of this work may be considered as based on the foregoing lists. This preliminary part, Part I, is based on the subjects in lists 1 to 4, and the data and conclusions of Part II are classified according to list 5. This method of presenting the data of Part II, was selected rather than list 1, Corrosives, because it makes the presentation simpler and less awkward from the economic angle. To many readers, a classification according to List 1, Corrosives, would seem more logical and useful.

The writers themselves agree that such a presentation would be better could it be done. We have found, however, that present knowledge of the subject has not reached an ideal enough state that such a presentation can be made. If, for instance, present practice in regard to handling any specific corrosive is described as correct, then progressive students who have

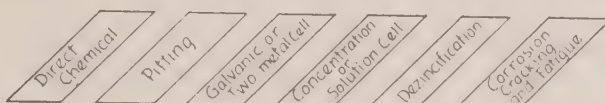
1. CORROSIVES

Metals are corroded by several different conditions as listed below:



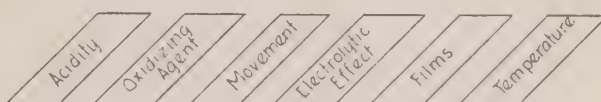
2. FORMS OF CORROSION

Visual inspection or mechanical examination of the corroded materials usually indicates that the corrosion has proceeded according to the following forms:



3. RATE FACTORS

Possibly the most important feature of corrosion is the rate at which it proceeds. This rate is determined or at least affected in most cases by the following more or less measurable factors which exist during the progress of the corrosion.



4. METAL CORROSION PROPERTIES

The attack of corrosion on the metals depends somewhat on certain properties of the metals some of which are typical of the metals themselves and some of which depend on its particular form while corroding.



5. METALS

Corrosion takes place on metals and for completeness the classification of metals according to their corroding properties or tendencies is given below:



Figure 1. Classification of Corrosion

ideas for improvement will say the practice of tomorrow will be different, and that the practice of tomorrow is the correct one rather than that of today. In most cases we find that there are several schools of thought on such matters. On the other hand if we take, as has been done, the actual data as obtained on the metals themselves, each engineer or industrial chemist has the opportunity of judging how much these data mean from a practical standpoint and can determine for himself a conclusion which suits his particular problem. Therefore, although this presentation is not ideal, we are convinced, after thorough study of the situation, that it is more practical than would be an attempt to come closer to the ideal.*

In order to bridge the gap practically, reference to the index will enable the reader to refer quickly and thoroughly to the data which apply to his problem.

* See also Introductory Statements to Part II, page 99.



Chapter I

The Rate Factors

The many concepts which are outlined in the Introductory Chapter in their relation to corrosion each bear a definite relation to all the others, and are so intertwined in their effects that it is difficult to separate them for description. The clearest method seems to be to first take up the central group, the rate factors. These concepts seem to be in the heart of the corrosion mechanism as the rate itself is the keynote of its economic effects.

These six rate factors are often all involved in one case of corrosion and it is safe to say that more than half of them are involved in every case of corrosion. Other factors, of course, often affect the rate but no others recur as important factors so regularly as these six.

In most cases, if consideration is given to these six factors, they will lead to a useful diagnosis. They are practical concepts to use for diagnosis because they are susceptible of measurement or at least of detection by instruments or observation. In any one case, it will usually be found that certain of them are more or less predominant and others can almost be ignored. They are roughly equal in importance in that any one or any combination of several may be the controlling conditions in a specific case.

To consider these factors in order:

ACIDITY

The possibility of a metal dissolving by a direct reaction with acid and replacing the hydrogen ion by metal ion with production of gaseous hydrogen is obvious. The type reaction in probably its most common form is:



This is one of the fundamental reactions of corrosion, and as such it must be thoroughly understood by anyone intending to study the theories. For full theoretical discussion of this reaction, the reader should consult the standard works on theoretical chemistry. Also Speller⁸ and Evans² have discussed the relations of this reaction to corrosion and much valuable information can be obtained by the student of corrosion in reading these works.

This pure type reaction is of more practical interest as combined with others than as an independent single reaction because in many non-ferrous corrosions where hydrogen is evolved as a gas, as in this reaction, rates are so high that they become of academic interest only. In other words, the evolution of hydrogen often indicates that, from a practical standpoint, continuous contact of that particular combination of corrosive and metal is impossible. (Nevertheless hydrogen is evolved in such an important case as pipe-line corrosion in acid soil).

This type reaction is, however, widely active in practical corrosion work as a part of the general corrosion mechanism. The physical chemist readily understands that while the reaction may not go forward itself, its energy relations may be such as to form part of a more complex reaction. It is thus often like a force, insufficient of itself to lift a weight, but active when sufficient additional force is applied.

An understanding of the fundamental ionic definition of an acid ⁶—a compound which produces *hydrogen ions* when in solution in water—is helpful. One of the definition properties of *hydrogen ions* is their tendency to be replaced by a metal; the reaction products being a salt of the metal and hydrogen gas.

The most interesting functions of this acidity reaction, considered as a corrosion factor, are in conjunction with other factors, for instance oxidation. The presence of free acid in contact with a metal, however, must always be thought of as a force tending to produce corrosion; it may be able to corrode the metal itself or it may be able to act only in conjunction with other forces.

OXIDIZING AGENTS (dissolved air)

By definition ⁷ oxidation is the increase in valency of an element and the presence of any oxidizing agent therefore produces the tendency for any metal, whose valence is zero to corrode or change to a compound where it has a positive valence. This tendency is in the same direction as that of the acid reaction, that is to change the metal from the uncombined state to a combined state with resulting complete change of physical properties. Therefore any oxidizing agent may be considered a corroding agent by definition.

By far the most common oxidizing agent is oxygen of the air and it is the greatest corroding agent. Its action is usually either in solution in water with or without other chemicals, or at high temperatures. The possibility of atmospheric oxygen entering into a corrosive action with the most telling effect should never be neglected in considering corrosion. This applies to the action of even the strongest acids and chemicals, though it is most evident in otherwise mild corrosives.

One of the writers ⁹ in an early paper showed that in the case of Monel metal and copper in contact with hot sulfuric acid, the rate of corrosion was increased sixteen-fold when the acid was saturated with air, as against acid washed free from air by means of methane. A retabulation of these results is given in Table 1. Specimens moving at a rate of 15 feet per min. were immersed in a 6 to 10% sulfuric acid solution at 180° F.

TABLE 1.—*Monel Metal and Copper vs. Sulfuric Acid.*

Metal	Corrosion Rate—Mg. per sq. dm. per day	
	Washed with Methane	Air Saturated
Copper	43	1070
Monel Metal	64	701

Whitman and Russell ¹⁰ determined the effect of oxygen in acid solutions on the corrosion of common metals and alloys. Selected striking results calculated from Whitman and Russell's figures are given in Table 2. Test pieces $1\frac{1}{8}'' \times 3''$, surfaced with No. 0 emery were used. The solution, at room temperature, was stirred by a gas-distributing device.

TABLE 2.—*Metals vs. Acids, with and without Oxygen.*

Metal	Acid	Corrosion Rate—Mg. per sq. dm. per day	
		Hydrogen Saturated (No Oxygen)	Oxygen Saturated
Mild steel	6% Sulfuric	1700	20,000
Lead	4% Hydrochloric	1350	13,000
Copper	4% Hydrochloric	1050	86,000
Tin	6% Sulfuric	350	43,500
Nickel	4% Hydrochloric	370	27,000
Monel metal	2% Sulfuric	60	5,700

No significant acceleration was found in the case of stainless steel and aluminum.

Fraser, Ackerman and Sands ³ showed that the effect of oxygen in the corrosion of Monel metal by sulfuric acid was "a linear function of the concentration of oxygen, and hence of its partial pressure,—except for concentrations approaching zero." This is illustrated in Figure 2, as taken from the above paper.

The presence of oxygen, or other oxidizing agent, may have exactly the opposite effect from that illustrated. It may produce a cathodic or passive effect and thereby reduce the corrosion rate. This effect is noted particularly on certain metals, as for instance, aluminum and stainless steel. It is also more liable to occur with certain acids and oxidizing agents than others. It has been noted on steel and nickel in sulfuric acid and on bronzes in mine

waters. A graphic representation of this effect is given in Figure 3, which shows the startlingly contrasting results obtained by adding air or nitric acid to sulfuric acid in contact with 18-8 stainless steel and Monel metal.

This apparently paradoxical behavior of oxygen and other oxidizing agents is not in disagreement with the chemical facts. The means by which oxidizing agents accelerate corrosion is through the cathodic part of the basic corrosion reaction given above. The mechanism and inherent harmony of these two effects is apparent when the electrolytic factor is analyzed.

MOVEMENT

Because the corrosion reactions take place on a surface, the contact zone between the metal and the corrosive tends to change in concentration immediately when corrosion starts. If the products of corrosion have any effect in later reactions this change in concentration may change the entire course of the corrosion reactions since this relative concentration change is very large. Movement of the solution will bring the concentration back to its original value or near it, depending on the relative rate of movement and corrosion. If the movement is relatively swift, it may prevent the formation of either the massive type or the thin cathodic solid films which would otherwise change the course of corrosion.

Where the concentration of corroding agent is low, its concentration in the contact region will be changed considerably by the progress of corrosion

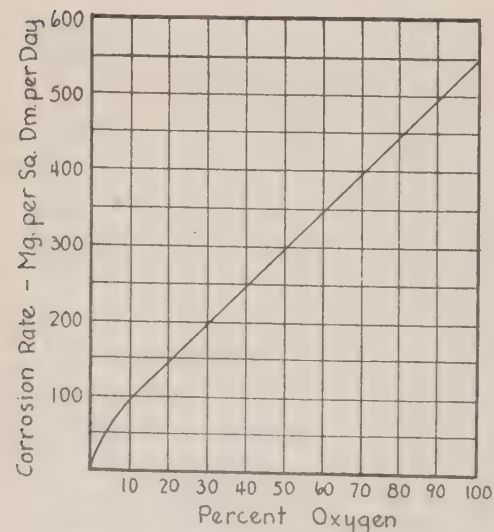


FIGURE 2. Influence of the Oxygen Concentration on Corrosion Rate of Monel Metal in 5% Sulfuric Acid.

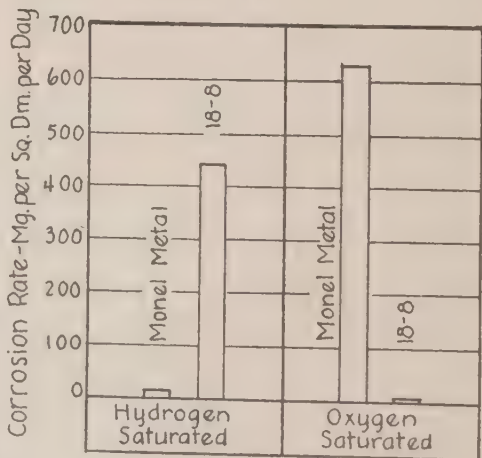


FIGURE 3. Influence of Oxygen on Corrosion Rate in 3% Sulfuric Acid.

and in this case movement allows corrosion to proceed where it might otherwise be quite slow due to low concentration. Since the most widely distributed corroding agent, oxygen, is very sparingly soluble in water and solutions, it is usually present only in low concentrations. It is rapidly removed from solution by corrosion. So it follows that the movement of solution is almost the determining factor of the amount of this most widely distributed agent which reaches the surface of metals. Movement also has a determining effect through its action on concentration or solution cells. High rate of movement tends to prevent the formation of such cells while a low rate tends to produce them.

Thus it is seen that while movement only acts indirectly through the other factors, it produces as widely variant a series of results as any other.

ELECTROLYTIC EFFECTS

One of the most characteristic phenomena of corrosion is its tendency to localize. A common observation of a corroded surface is its roughness and on the other hand seeing a rough metallic surface, a very common deduction is that it has been corroded. This tendency to roughen, corrode locally, and pit is often due to electrolytic effects. Where one area is corroded to the exclusion of others the cause is usually electrolytic corrosion.

By the now universally accepted electrochemical reasoning on the mechanism of chemical reactions, any reaction including the corrosion reactions may be divided into two parts which may be called anodic or cathodic according to whether the electrodes absorb or give up electrons. For instance, in the reaction between iron and sulfuric acid, we can say that the anodic part of the reaction is the solution of the iron as ferric ion which is accompanied by the giving up of electrons to the electrode. The cathodic part is the hydrogen ion going out of solution becoming hydrogen gas with the absorption of electrons from the electrode. The combination of the two is the replacement of hydrogen in solution by iron with corrosion of the iron and evolution of hydrogen gas. This reaction may take place at one point, the hydrogen appearing where the iron is corroded and then the reaction is a simple chemical or electrochemical reaction. But in a highly conducting acid solution and on the surface of an iron plate of appreciable thickness so that the electricity may be conducted easily (electrons pass freely) there is little to hold the reaction together and if something occurs which makes it easier for the anodic and cathodic parts to take place at different points, this is very prone to happen. Where reactions occur which are more complicated than the above example, there are many conditions which may cause the reaction to take place in two parts. The two commonest are mentioned here.

The one which has been longest understood is commonly called galvanic action, due to the presence in electrical contact of two metals of different tendency to go into solution. This may occur by difference in composition of an alloy, physical non-homogeneity of a single piece of metal, or by electrical contact between two entirely different metals.

The other which has been demonstrated only in recent years has been called concentration cell action and is due to the presence of the active corroding material in different concentrations at adjacent areas on the surface of homogeneous metal, or the adjacent presence of two different corrodents. Since this latter phenomenon was first described ⁵ it seems to clarify more and more of the previously obscure corrosion phenomena, and it now appears to be a factor even more important than the more familiar galvanic effect.

Whatever the mechanism of the separation of the two parts of the reaction, the electrolysis is the factor which most often determines the place at which corrosion occurs. It does not, however, change the fundamental reactions by which corrosion occurs and it is itself tremendously affected by all the other principal factors.

SOLID FILMS

The whole corrosion reaction takes place on a surface. When the reactions of corrosion supply a product which is insoluble and which can form a solid impermeable film or a film which has any properties which are appreciably different from those of the corrosive solution, such a film has a tremendous effect on corrosion.

Films are roughly divisible into two groups according to their properties and effects. First, the easily visible films of corrosion products which are insoluble in the solution. These are usually easily permeable by water but sufficiently dense to considerably cut down the flow of fresh corrodent to the metal. These films may cause corrosion to slow up to a certain extent by retarding contact of the corroding solution with the metal. On the other hand, their action is often deleterious in speeding up corrosion in certain areas by electrolytic concentration or solution cell action and in atmospheric corrosion by causing the retention of moisture. They are liable to be non-uniform or even discontinuous and when this is the case they allow the active solution to come into easy contact with the metal in certain areas while partially screening it in others. This is an ideal way of producing electrolysis. The part under the partially permeable film usually becomes anodic and pitting or local corrosion commences there while that part which is exposed is cathodic. The corrosion produces more of the same type of film which strengthens the electrolytic cell and thus the deepening of the pitting is self-sustaining.

These films may also contain corrosion products which are slightly soluble in the solution so that they are in themselves corrosive. When present in atmospheric corrosion, they may be hygroscopic and by retaining moisture at humidities in which the metal surface would otherwise be dry they will increase the corrosion rate many times.

The second class of films is the cathodic or passive film. Their properties have been studied and classified by several competent men. U. R. Evans² was the first to give these films concentrated study and to explain how they act in corrosion. They have the same effect as the cathodic part of a concentration or solution cell in that they allow electric current to pass into the metal (the metal giving up electrons) but prevent or resist passage of ions thus preventing the flow of current in the other direction. The films are believed to thoroughly cover the cathodic areas in the type of corrosion which Evans calls the Differential Aeration Cell, and where they are absent the metal is anodic and is corroded. In the nature of their action they must be thinnest where they are most protective and this explanation is proved by observation because the films are so thin as almost to resist measurement when their protection is complete. E. C. Hedges⁴ has compiled a wealth of data and proof of the composition and detailed properties of these films. They are principally oxides which have certain unusual properties associated with the thinness of those which are most protective. They may vary somewhat in composition and have varying effects on corrosion rates (See also Chapter IV—Oxidation Passivity).

TEMPERATURE

Temperature is one of the controlling rate factors in all chemical reactions. It thus enters into every corrosion reaction by speeding up the natural rate of reaction as the temperature rises. This speeding up may be closely parallel to the energy relations as they affect the rate of reaction but it is more usually affected also by other factors so that its effect may be greater or less or even opposite. Rise in temperature increases ionization and increases the mobility of all reacting bodies. It increases diffusion rates and lowers viscosity.

Temperature difference may have an important effect through its effect on films. Films that form at one temperature may not form at another. Change in solubility of the films may be so great that those formed at one temperature may dissolve at a higher one. Local differences in temperature may set up electrolytic cells which may be considered either galvanic or concentration cells.¹

The change of rate with temperature is usually in line with the ordinary limits of reaction velocity (say double to four times the rate for a rise of 50° F.) or it may be many times this or be negative in effect when it causes

such powerful secondary effects as the removal or production of protective films.

EXAMPLE

As an example of the operation of some of these rate factors, consider the action of sulfuric *acid* on a copper tank. Assume a closed cubical tank one meter each way. The area of the tank inside is six square meters and it will hold 1000 liters of acid. If *air*-saturated 2% *acid* is put in the tank at about 140° F. corrosion will start at a rate of 1000 mg. per sq. dm. per day. Copper will be dissolved at the rate of 600 grams per day and if this rate were continued a tank $\frac{1}{8}$ " (.32 cm.) thick would disappear in about 9 months.

However, if the acid is put in and the tank completely closed to *air* contact the *air* would all be removed in a short time. About 10 grams of metal would be dissolved and then the reaction would stop from lack of *air* and the tank would last indefinitely. If corrosion proceeded at the initial rate the *air* would be exhausted and corrosion would stop in 25 minutes.

If the hot acid were run through the tank at a fairly *rapid rate* the tank would be ruined in less than 9 months as above. If the *temperature* were room temperature, say 60° F., the same reaction would require about 36 months. If the *air* content were reduced to that ordinarily present in acid contact with metal the time would be 5 years and if there was practically no *movement* of the acid it would require 15 years for complete solution. In actual practice *films* of solid corrosion products would probably form which would induce *concentration cells* and possibly *galvanic cells*. Failure from this cause might occur in a few weeks or be delayed for years depending on more or less chance distribution.

THE RATE FACTORS

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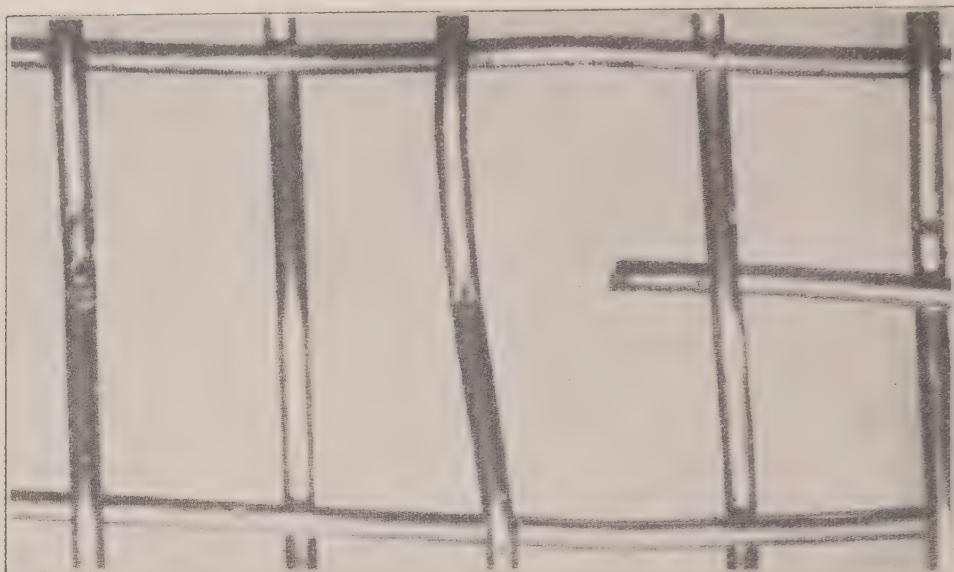
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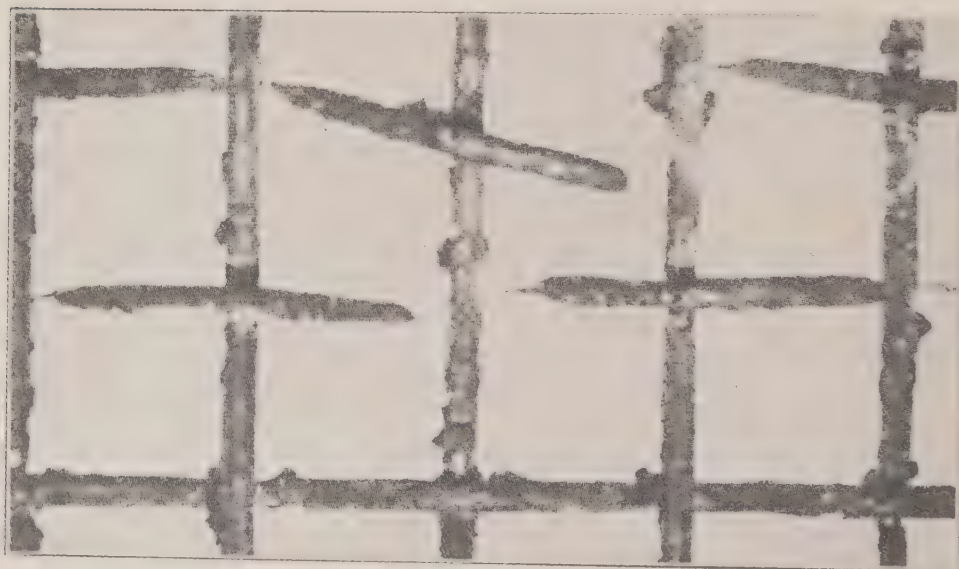
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Beginning of Corrosion



Final Failure

SOLUTION CELL CORROSION

The areas at junctions between wires are mechanically protected while the adjacent areas are in free contact with the corroding solution. The junctions become anodic and corrode.

Chapter II

Forms of Corrosion

Examination of metals during corrosion or after it has occurred may indicate much about the cause of the corrosion and why it continues. It should include macroscopic examination of the surface with the corrosion product in place and also after the corrosion product has been removed. This should indicate in most cases the general "form" of the corrosion; that is, whether it has been a *direct chemical* action, a *pitting*, *galvanic* action, *concentration cell* corrosion, *dezincification*, or *corrosion cracking* or *corrosion fatigue*. Of course, several of these effects may take place at the same time but it is usually the case that where failure has occurred it is directly attributable to one of these forms with possibly some help from a second. Each one of these forms is accompanied by typical signs which are not difficult to read with a little experience. These signs will be described in connection with a discussion of each form. In making laboratory or service tests it is always desired to make a diagnosis as rapidly as possible. It will often be a matter of some difficulty of judgment to decide which one of the various forms which exhibit themselves in the early stages, is the one which will cause the final failure. Many of the mistakes which are made in evaluating corrosion tests are due to failure to make such judgment correctly. For instance, it is a mistake to assume one metal better than another or one condition less harmful on the basis of loss of weight, which is a good measure of direct chemical corrosion, if the final failure is to be by pitting rather than by direct chemical corrosion. This holds true for each of the forms considered. Each has its own measure and the correct one must be selected from the five others to judge values correctly.

DIRECT CHEMICAL

There are a large number of chemical reactions in which a pure metal may take part where the end products are non-metals. Each of these myriad reactions will produce corrosion if allowed to proceed at the surface of a metal. There is no more mystery about why and how they will proceed than there is about why and how any chemical reaction proceeds, with the exception that the space arrangements are far from being as perfect

as in a simple chemical reaction like pouring the solution of one reactant into the solution of another. The engineer who is interested mainly in corrosion rate and design to resist it can well accept the theories of the theoretical chemist on the one hand and of the theoretical metallurgist on the other as to the mysteries of these reactions, and for a true understanding of the corrosion problem simply be sure that he understands how the accepted theories work together to produce the particular corrosion being considered.

When a metal is in contact with one of these many reactants with which it may combine to form a non-metal or to precipitate another metal, corrosion will proceed at a rate determined by the combination of "rate factors" described above. If none of the other "forms" is present, we then have the simplest and the most fundamental kind of corrosion. The action is relatively uniform over the whole surface of the metal and proceeds at a fairly uniform rate as the metal is corroded.

The appearance of the surface of the metal being corroded in this manner will be relatively smooth but obviously "etched." The color of the surface will be the same as that of a freshly ground surface of the same metal. This surface appearance is an indication that the corrosion is of the direct chemical type unless other signs are present as described later.

A common example of this type of corrosion is the action of a good pickling solution on any metal. These solutions besides dissolving or otherwise removing the oxide will leave the metal surface itself etched clean and smooth.

The loss in weight of the metal per unit of surface per unit of time is a good easy method of determining the rate of this type of corrosion.

The most common condition causing this type of corrosion is an acid solution in contact with the metal. Oxidizing agents in the solution may speed up the reaction without introducing other forms of corrosion if they are not present in too high relative concentration or activity. If any solid corrosion products or other surface films are formed they will interfere with the uniform action and if conditions tending to produce measurable electric currents are present they will localize the corrosion. Although, under such conditions, the direct chemical action may still go on at an undiminished rate, the local corrosion is likely to be the most serious cause of failure. Measurement of the weight loss will only serve to measure the corrosion if localization happens to be also measurable or uniform for the existing variations of time and conditions.

PITTING

Corrosion is often localized in well-defined areas and where such areas are relatively small as compared with the whole metal surface, they are

spoken of as pits. A pit is usually distinguishable by a relatively sharp or well-defined boundary around part or all of its perimeter. This may be just a sharp change in the direction of an otherwise level surface but the boundary is more usually a wall which approaches the perpendicular to the surface and in many cases it may be undercut or so irregular that the surface or intermediate parts of the wall extend out well over the bottom of the pit. Intergranular pits may extend in a honeycomb shape like the complicated caves of a limestone region.

Pitted metal commonly has a speckled or irregularly dotted appearance. Pitting is usually accompanied by the formation of solid corrosion products which are usually irregular in appearance with probably the thickest sections over the pits. A dotted appearance of the corrosion product or a surface with well defined irregularities is liable to be an indication of pits underneath. When the corrosion product is cleaned off it will often have a tendency to cling in the pits even to a greater extent than would be expected from the purely mechanical difficulty of cleaning out such a confined space. An otherwise clean uniform surface may contain pits which are full of adherent corrosion product.

Pitting as a general head is allied very closely with other subjects in this outline; these subjects are indicated below and the reader should refer to them for a more complete description of the relation of each to pitting.

Pits may be formed by a protective corrosion product which partially covers the surface so that certain areas are exposed to repeated action of the corroding agent. Pits occur on the exposed areas. While this action is not unusual and is easily diagnosed, it is not one of the most common causes of pits.

The second cause in practical importance is probably the presence of inhomogeneity in the metal. If the metal contains inclusions of a more easily corroded metal, the latter may corrode galvanically or directly at a more rapid rate and so form a pit. If there are inclusions more cathodic than the body of the metal these inclusions induce pits in their neighborhood galvanically. If there are inclusions permeable to moisture or otherwise, such as to leave a pocket which can contain corroding agent different in composition from the body of the corrodent, concentration or solution cell pitting may occur.

This latter most common form of pitting may start as an inclusion or may start from exterior factors. Because it is usually self-perpetuating rather than decreasing in intensity by its own action, like the other forms of pitting, it is probably the most destructive. It is more fully described under its own heading and the reader is urged to study that part carefully if he wishes to really understand the pitting phenomenon.

A fourth cause of pitting is inhomogeneity existing in the metal from some other cause than inclusions. This may be uneven distribution of strains, particularly such strains as cause near or incipient parting of the metal, or dendritic or granular segregation of the constituents. While this cause may not be as widely distributed, if all corrosion is considered, as some other forms, it is of extreme importance where it does exist and in environments where it has been found to occur it should always be looked for carefully as the tendency may exist with little obvious or measurable indication.

Pitting is measured by actual micrometer measurement of the pit depth with an instrument having a properly shaped tip, or by a calibrated high power microscope focusing on the surface and then on the pit bottom. Qualitative measurement may be made by examination of properly prepared sections or by the x-ray. Weight loss is of little help and tensile tests may be somewhat misleading though they do give indications in the proper direction. This most destructive form of corrosion is possibly the most difficult of experimental evaluation.

TWO-METAL GALVANIC ACTION

The first-discovered and simplest mechanical form of electric cell consists of two metals connected with each other and immersed in a single solution. The result is well known. The action of the cell depends entirely on the different chemical properties of the two metals. The term has been broadened by some physical chemists to include cells wherein the presence of different solutions affects the results. In corrosion literature, however, it has been the practice to limit the term to its original meaning which does not include solution differences and to call cells caused by solution differences concentration cells.*

It should be noted that the concentration or solution cell produces the same effects, in many cases, as the two-metal galvanic cell. The two forms are interdependent and in the more detailed discussion under "Concentration or Solution Cells" their relation is described.

1. *Definition:* Two-metal galvanic corrosion is rapid corrosion of a metal due to its being electrically connected to another metal in corrosive conditions. The cause is the difference between the individual tendencies of metals to be acted on by (combine with) corrosive materials. By certain arrangements this difference in tendency of two metals to corrode can be measured in volts. This voltage of the cell is the driving force behind the corrosion.

2. *Galvanic Series:* Arranging the metals according to their tendency to corrode galvanically results in the following approximate order.

* The appropriateness of these terms is discussed further under the concentration cell heading.

Note that this is not an "Electrochemical Series" but, due to the fundamental chemical affinities, that it has some general analogies with the "Electrochemical Series."

Corroded end (anodic)

Magnesium
Aluminum
Duralumin

Zinc
Cadmium

Iron
Chromium iron (active)
Chromium-nickel-iron
(active)

Soft solder
Tin
Lead

Nickel
Brasses
Bronzes
Nickel-copper alloys
Copper

Chromium-iron (passive)
Chromium-nickel-iron
(passive)

Silver solder

Silver
Gold
Platinum

This series is built upon actual experience with corrosion and laboratory measurement. Metals grouped together have no strong tendency to produce galvanic corrosion on each other; connecting two metals distant on the list from each other tends to corrode the one higher in the list. Voltage figures are not given because these vary with every new corrosive condition. Relative positions of metals change in many cases but it is unusual for changes to occur across the spaces left blank. The chromium-irons and chromium-nickel-irons change position as indicated depending on oxidizing conditions, acidity, and chloride in solution. The series as it stands is correct for many common dilute water solutions such as sea water, weak acids and alkalies.

Protected end (cathodic)

The above series shows the tendency to corrode, but actual galvanic corrosion takes place only when current flows. To allow current to flow certain conditions are necessary as follows:

3. *Conductivity.* The circuit must be complete through conducting metals and solutions. Metals are usually good conductors and allow easy passage of current, but serious resistance may develop in the solution and in the metal contacts. Distilled water and air are such poor conductors galvanic corrosion is unusual in them. The presence of slight impurities and salt in water, as in ordinary tap water, makes it sufficiently conducting to produce some galvanic corrosion. Stronger salt solutions, as sea water, are good conductors, and concentrated solutions of salt and chemicals, particularly strong acids and alkalies, are very good conductors, and galvanic

corrosion is common in them. Current may pass short distances through damp films of corrosion products or condensed moisture.

Metal contacts in ordinary types of metal seams are good enough to allow galvanic corrosion to take place. Accumulations of dirt or corrosion products may slow up the corrosion. This has occurred in bearings. Joints may be insulated by rubber, fiber or wood so as to prevent galvanic action completely. Insulation must be absolute and not allow any metal path for the current.

4. *Contact Surface*: Galvanic action often produces gases (hydrogen) and corrosion products which prevent contact. Rapid flow which removes these impediments or chemicals which react with them increase two-metal galvanic corrosion. (Stagnation may produce solution concentration cells which are as active as the two-metal cells.) There are many changes which take place at corroding metal surfaces when current flows. Formation of hydrogen gas at the protected surface is common, also formation of insoluble protective films on either protected or corroded surface.

Interference with passage of currents by such films or by chemical changes is called polarization. Chemical changes take place in the contact films of solution, sometimes lowering its conductivity and sometimes producing independent currents which may oppose and reverse the original one. These changes usually oppose the original effect. These effects are some of the most important factors governing galvanic action but are too complicated to describe fully here.

5. *Proximity*: Surfaces must be close together. Where sheets meet at an edge all galvanic corrosion will be close to the seam, except in electrolytes of the highest conductivity.

6. *Large Cathode Area*: A large area of protected metal produces more rapid corrosion on the metal corroded. Small anodes are rapidly corroded. In good conducting solutions a steel rivet in copper or nickel alloy sheet is rapidly corroded but a copper or nickel alloy rivet in steel sheet will produce little corrosion except at the contact.

7. *High Voltage*: Large differences in voltage, *i. e.*, distance from each other in the series list, tends to produce more rapid corrosion, but this effect is liable to be masked by 3, 4, 5 and 6.

CONCENTRATION CELL OR SOLUTION CELL

This type of corrosion has come to be accepted in a somewhat limited circle of engineers and corrosion students as one of the important "forms." In the experience of the writers and their colleagues it has been of much value in diagnosing and preventing corrosion. However, it has not had such complete experimental study and description in the literature as has, for instance, the galvanic cell or the "differential aeration" (or film) cell.

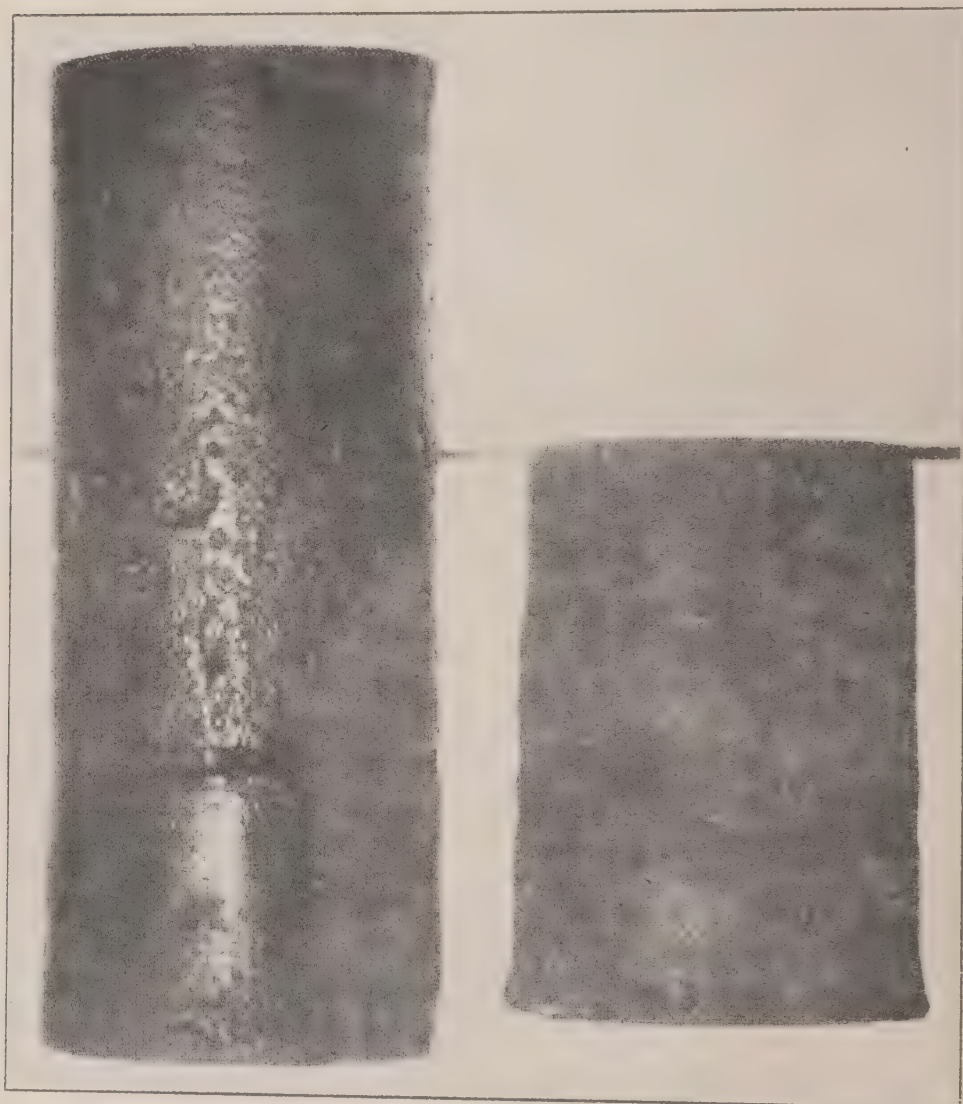
therefore seems necessary to assign rather more space and emphasis to it in this work than its relation to the other "forms" of corrosion would warrant.

Electrolytic *vs.* direct chemical corrosion: Corrosion may take place by direct reaction between the metal and the solution in contact with it, or the corrosion reaction may separate into anodic and cathodic parts which may take place at areas separated from each other by finite distances. If the reaction takes place without separation, it is called *direct chemical* corrosion and if the two parts are separated it is called *electrolytic* corrosion. Whether it is direct chemical or electrolytic, the course of the reaction must be in conformity with the known laws of electrochemistry and thermodynamics.

The separation of the reaction into two parts happens readily because the metal is a conductor. Separation often becomes necessary to the progress of the reaction because of the effect of the corrosion reaction on the plane of contact. The compounds of the metal formed are often rather insoluble and the contact film of corroding agent may become saturated and precipitate corrosion products. Thus the solid products of corrosion often prevent free contact of the corrosive with the metal soon after corrosion begins. But for electrolytic corrosion, it is not necessary that contact be made at the same point where metal is corroded. According to the principle of the *concentration* or *solution* cell the metal goes into solution or combination at one point when the best contact with the corrosive solution is at some other.

The Relation of Galvanic to Concentration or Solution Cell Corrosion

When the principles of electrochemistry were still new in their practical application to chemical and metallurgical phenomena W. R. Whitney¹⁴ suggested the hypothesis which was called for some years the "electrolytic theory of corrosion." This theory in his own clear words was as follows ". . . the theory requires that iron should *tend* to oxidize in any aqueous solution. Whether it will do so or not depends on other conditions. Something may here be gained by a study of analogies. The dissolving zinc electrode of the Daniell or gravity battery, although possessing an enormous electrolytic solution-pressure, does not dissolve when the electric current is broken, but begins oxidizing immediately when connected through an external resistance to the copper pole. It is not enough then for oxidation or solution of the metal, that it have a *tendency* to dissolve; it must be in metallic connection with some other material capable of acting as an electrode, and this second electrode, if a positive element must have a lower electrolytic solution pressure than the iron. Iron in contact with zinc and



SOLUTION CELL CORROSION

Bottom part of tubes from separate evaporators. Each was set in a tube sheet of the same metal as the tube. A layer of corrosion product and debris on the tube sheet around the tubes partially separated a small circumferential area from corrosive solution causing anodic corrosion on shielded area.

an aqueous solution will therefore not dissolve; but if copper replaces the zinc, the iron will dissolve, the velocity of solution in these cases being determined by the resistance of the complete electric circuit." This was the first recognition of the all important fact that the ordinary corrosion reaction was divisible and does often divide into its anodic and cathodic parts. Later workers showed that atmospheric oxygen^{10, 11, 12} entered into the reactions by "depolarizing" or uniting with hydrogen at the cathode and even that high concentrations of oxygen caused iron to become cathodic and to corrode anodically at surfaces of low oxygen concentration. This, in conformity with Whitney's hypothesis, Aston¹ explained on the basis of its influence on "the polarity of the underlying iron." It now seems that this early view put rather too much emphasis on the electrodes themselves of the galvanic cell. This emphasis left many phenomena, recognized as electrolytic corrosion, partially unexplained.

The Concentration or Solution-Cell Principle

An electrolytic corrosion cell may be developed by:

1. Two different metals in the same electrolyte.
2. Two metals in different electrolytes.
3. The same metal in two concentrations of the same electrolyte.
4. The same metal in different electrolytes.

The first condition is the ordinary galvanic cell.^a The third one is an example of the concentration cell of the physical chemist which, by its susceptibility to exact measurement has contributed greatly to the quantitative knowledge of chemical energy.^{6, 9}

Besides the first type or the two-metal galvanic cell, the other three types of cells are also active in producing corrosion. In 1922 and 1924 one of the writers^{7, 8} measured the potential of a corrosion cell of the pure concentration type and determined that many other cells besides the simple galvanic could cause corrosion. The term "Electrolyte Concentration Cells" was used to distinguish them from the two-metal galvanic type, but this term is rather misleading because it is commonly applied to the reverse concentration cell of the physical chemist.^a The corrosion cells should not

^a The concept of Galvani and Volta, the first students of these cells, did not include the effect of different electrolytes. From this standpoint the term galvanic might properly be limited to the two-metal cell and this two-metal cell is the thought generated in the mind of the average layman by the term. However, modern physical chemists in broadening the concept to include the types listed above, and other types also, have broadened the use of the original term to include all the types. While this is logical for these scientists, the complete concept is not as simple for the non-chemist as is the two-metal cell and therefore a new term would be a useful aid to expression.

The term "Concentration Cell" might logically cover the additional thought if we were to extend "Concentration" to include "Zero Concentration." But usage is distinctly against this as the term currently is applied to just those finite concentrations which are susceptible of measurement and calculation. Possibly "Solution Cell" as opposed to "Metal Cell" are terms which are sufficiently distinctive to be readily understood.

be thus limited. They include many cells involving quite different types of electrolyte and particularly electrolytes which do not contain the electrode metal as an original constituent. Possibly a more descriptive term would be "Solution Cell" or "Chemical Reaction Cell." Whatever the term used it should be understood that in these cells the potential difference is caused by differences in the solution rather than in the electrodes.

Evans, later,³ developed his thought on the "Differential Aeration" cell and has clarified many otherwise difficult corrosion problems by his interesting experiments and explanations. His theory involves the presence of a cathode film as the fundamental source of the potential difference.

The electromotive force of the solution or chemical cell is of the same order of magnitude as the two metal or galvanic cell. For instance, it is possible to reverse the usual direction of the zinc:copper couple by immersing the copper in potassium cyanide and the zinc in zinc sulfate. A cell of silver electrodes in silver solutions of readily obtainable concentration differences calculates and measures over .5 volt. The copper concentration cells measured by the writers⁷ gave potentials of .2 volt. E.m.f.'s of over 1 volt are obtained by varying the oxygen concentration in an acid solution on stainless steel electrodes (The action here is certainly aided by surface films).

In all electrolytic cells the action is due solely to chemical reactions at the electrodes. The e.m.f. of the cell is a function of the driving force or chemical affinity causing the reaction. The electrolytic corrosion is equivalent to the amount of current as measured in amperes, and this value at its maximum is the equivalent of the chemical change occurring in the electrolyte.

To make this clearer, the following diagrams (Figures 4 to 8) illustrate the reactions occurring in simple forms of the above types of cells.

FIGURE 4. Common Two-Metal Galvanic Cell.
(Long known as a corrosion stimulator)

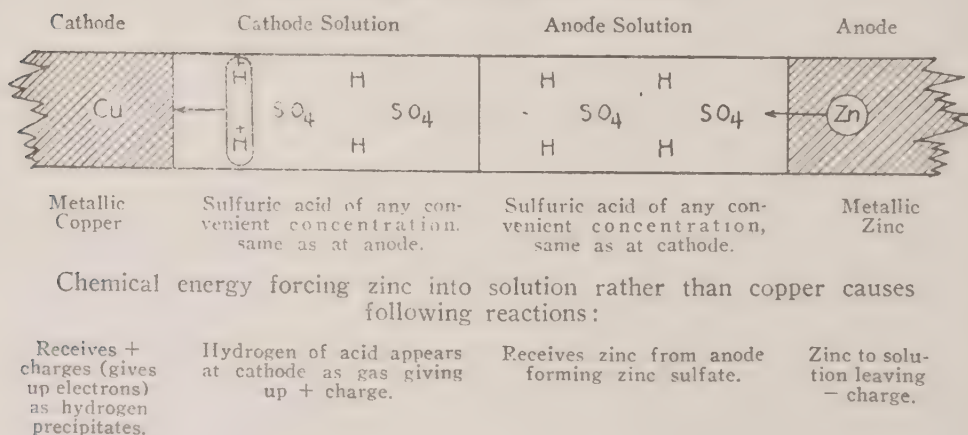
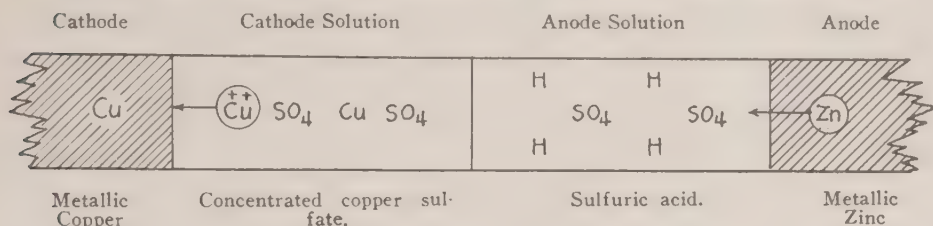


FIGURE 5. Two Metals in Two Electrolytes. The Daniell Cell.
(This cell acts more powerfully and with less interference than figure 4.)

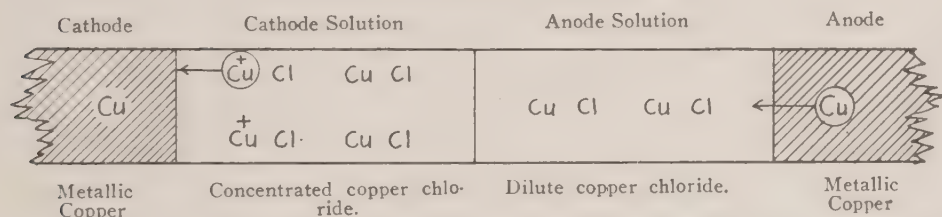


Besides tendency of zinc to dissolve there is pressure for copper to precipitate at cathode. Reactions below.

Receives + charges as copper deposits.	Copper deposits giving up + charges (receiving electrons) at cathode.	Receives zinc from anode forming zinc sulfate.	Zinc dissolves leaving - charges.
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(The above cell acts, but less powerfully, with both electrodes copper.)

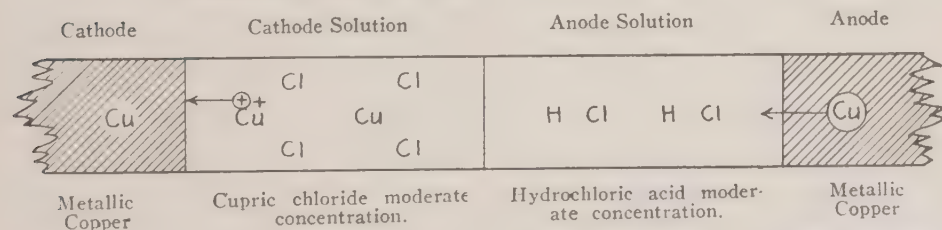
FIGURE 6. The Same Metal in Different Concentrations of the Same Electrolyte.
(A Reversible Concentration Cell.)



There is pressure to precipitate copper at the cathode and so remove concentration differences. Reactions below.

Receives + charges as copper deposits (is reduced)..	Gives up copper and + charges (receives electrons) at cathode.	Receives copper from anode forming copper chloride.	Copper dissolves leaving - charges.
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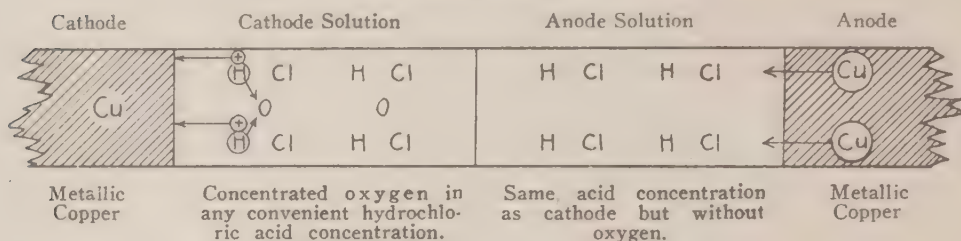
FIGURE 7. The Same Metal in Different Electrolytes.
(Often active where acid and copper alloys are in contact.)



There is a tendency for cupric ion to reduce to cuprous ion at the cathode. Reactions below.

Receives + charges as cupric copper is reduced.	Cupric chloride is reduced to cuprous giving up + charges.	Receives copper from anode forming copper chloride.	Copper dissolves leaving - charges.
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FIGURE 8. Simple Form of Oxygen Solution or Concentration Cell.
(Now recognized as very destructive.)



Chemical energy pressing for reduction of oxygen causes following reactions:

Receives + charges as hydrogen of acid reacts with oxygen (reduction).

Hydrogen from acid reacts with oxygen forming water, giving up + charges to cathode.

Receives copper from anode.

Copper dissolves leaving - charges.

The diagram represents a magnified section of the electrodes of a cell as connected through a uniform section of solution divided into anodic and cathodic parts. The usual chemical symbols are used to indicate compounds in solution and the concentration is roughly indicated by the number of symbols in the rectangular figure. Direction of reactions is indicated by small inclosures and arrows.

While the reactions given are correct they are much simplified and will thus seem incomplete to some. This license is justified for the convenience of readers not now specializing in chemistry. Competent critics can draw their own complete picture and thus satisfy themselves better than could we halting authors.

The illustrated oxygen cell is a simple type of a cell which occurs in practical corrosion with great frequency. The variations are complicated and have not been thoroughly studied. Certain points should be noted.

The solution or concentration cell is strikingly different from the ordinary galvanic cell in the fact that the direction of its current is in a sense inverted and throws the corrosion to a point which would not be corroded without the cell action. Thus, note that in the common galvanic cell, Type 1, before the anode and cathode are connected the zinc (anode) is corroded more than the copper (cathode). Now in the common oxygen cell, (and the other solution or concentration cells) note that if the connection were not made the greatest corrosion would occur in the oxygen-acid mixture (cathode) rather than in the pure acid (anode). This seemingly anomalous behavior is characteristic and of much practical importance in diagnosing corrosion by these cells.

In strongly acid solution the concentrations involved tend to neutralize and some convection or other artificial effect is necessary to cause the con-

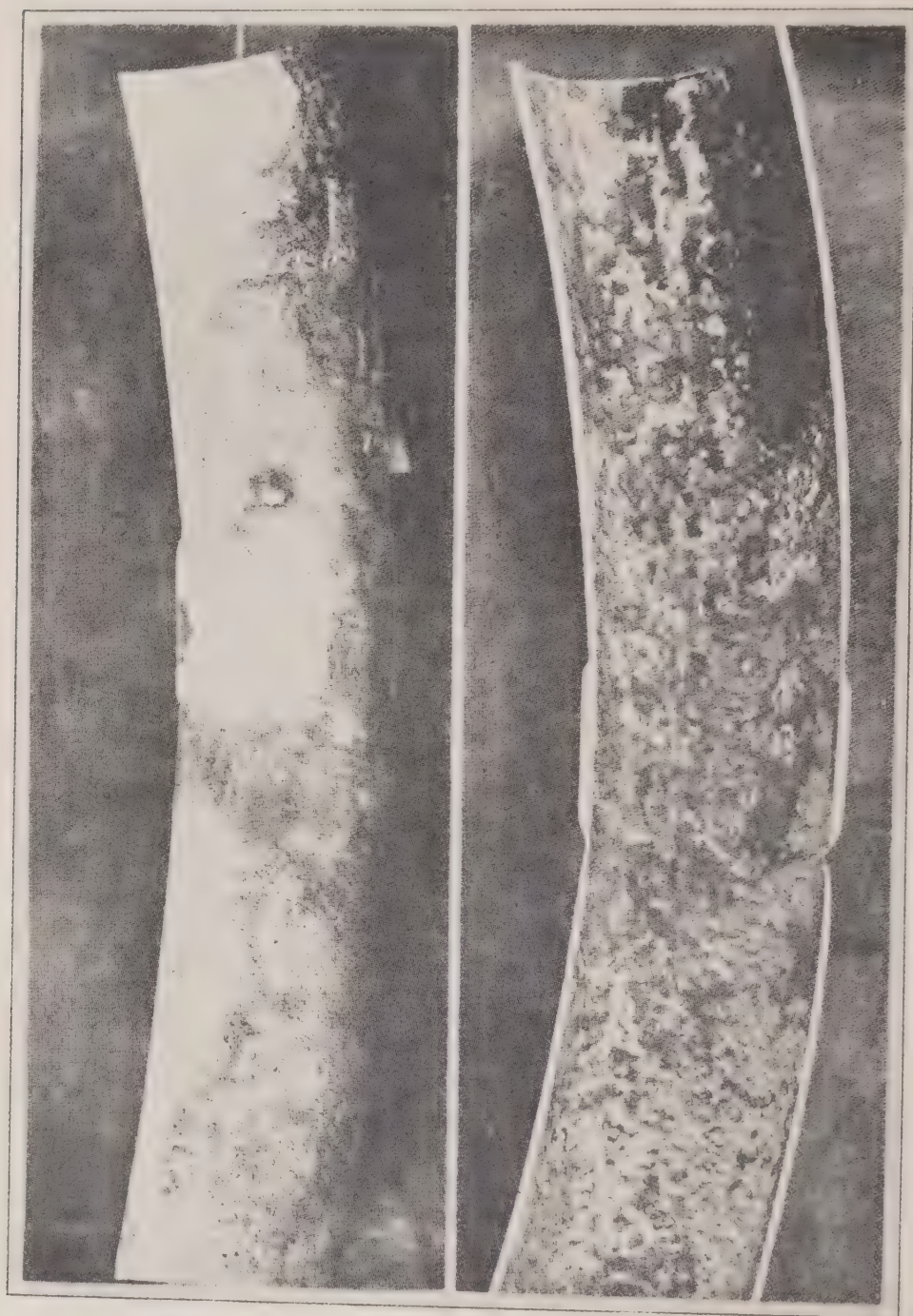
centration or solution cell to act. However, in the great field of slow corrosion in neutral solutions there is a common tendency for cells to localize and perpetuate themselves. The corrosion products easily become so concentrated as to precipitate and prevent free contact with fresh solution. This effect is enhanced by migration of the hydrogen and hydroxyl ion under the current which helps to produce insoluble basic salts near the anode. The original cathode area remains clean and therefore encourages the cathode reaction and in the absence of interference the corroding chemical is constantly replenished by convection and diffusion. It is thus seen that the slightest accidental variation in freedom of contact between metal and corrosive solution tends to become accentuated because the corrosion products produce physical interference at the point where the metal dissolves. This point, which was originally one of slightly poor contact, becomes progressively poorer while good contact continues at other points by diffusion and convection. The point of good contact with corrosive solution is the cathode and the point of poor contact where the metal dissolves is the anode. Electric current, of course, flows through the metal from cathode to anode. Obviously the anodic areas are formed more rapidly and positively when bulky insoluble compounds are the result of corrosion. Thus, corrosion tends to be electrolytic where corrosion products are insoluble and direct chemical where they are soluble. It tends toward electrolytic with low concentrations and little movement and toward direct with the reverse conditions.

Obviously any of the materials which will corrode metals may set up concentration or solution cells. The reactions will be the same as though the corrosion were a direct chemical reaction but they will be divided into anodic and cathodic portions and the direction of current will be from high to low concentration of the actual corroding agent.

Corrosion Cell Pitting

The copper ion cell and the oxygen cell are two common types of solution or concentration cells. But the formation of such cells is almost a necessary phenomenon wherever corrosion products are insoluble no matter what the corrosive agent or the metal concerned. Thus the effect of insoluble corrosion products in forcing the formation of cells is such that it is rather more logical to expect corrosion to proceed by pitting in many cases than by uniform attack.

The prevalence of pitting in the corrosion of even the purest iron has not been satisfactorily explained by the galvanic or voltaic cell, although it has been given much thought on account of its economic importance. This pitting is an example of the phenomena which seem to be completely



Surface

Section

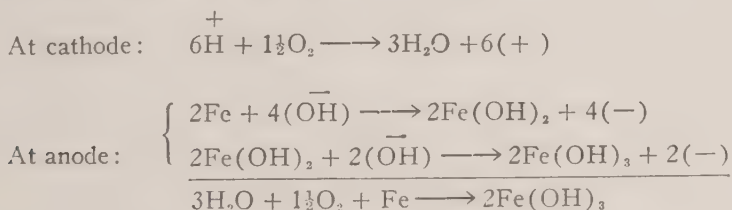
TWO-METAL GALVANIC ACTION

Part of Acid Heater Coil. The uncorroded central portion was tightly covered by the supporting member of a more noble metal than the coil. The areas near the edge contact of the noble metal are badly corroded galvanically while areas at a distance are only slightly attacked.

explained by consideration of the action of oxygen concentration or solution cells.

When iron comes in contact with oxygen-bearing solution it reacts with the oxygen and water, forming ferric hydroxide. The precipitate tends to flocculate, or may congregate in one point by settling or be distributed by currents in the solution. Where a mass of precipitate or other solid material is held by any chance in contact with the iron, the oxygen in the solution in the pores of the mass near the iron immediately disappears in reacting with the iron. In the region around this mass, the oxygen content is renewed by convection and diffusion, and we have a cell set up with a low concentration of oxygen in the mass of precipitate and a higher concentration in its neighborhood. The metal in contact with the higher concentration becomes the cathode, and that in contact with the low oxygen concentration in the precipitate, the anode. Iron goes into solution under the precipitate and the action is autocatalytic, as the longer it goes on the thicker the precipitated mass becomes and the more efficient as a diaphragm. A pit forms and deepens indefinitely. In the later stages, precipitation occurs as ferrous hydroxide and there is always a layer of ferrous hydroxide in contact with the metal. Quantitative results, showing the conditions existing in these circumstances, have been given by Whitman, Russell and Altieri.¹³

The reaction by which iron dissolves divides into three parts, which take place at different points, as follows:



The reactions assume the reaction of dissolved oxygen directly with the hydrogen ion of water without formation of hydrogen gas. Whether or not the hydrogen gas actually forms and the action of the oxygen is a depolarization, does not affect the final conclusions.

The mechanism in this case is especially adapted to cause pitting. The precipitate of iron hydroxides forms a physical separation between the two portions of this cell at its liquid-liquid contact. This action is essential in localizing the corrosion. The formation of ferric hydroxide also operates *chemically*, in two distinct ways, to accelerate the action. First, oxygen is removed by its reaction with ferrous hydroxide; and second, iron is removed by precipitation, which, if not removed, would retard the reaction by the mass law and would set up a counter e.m.f.

Effect of Corroding Film (Film Cells)

Many useful facts have been deduced from the modified explanation of the oxygen concentration cell given by Evans.³ The modification consists in the introduction of an oxide film on the cathodic areas, as a necessary adjunct to the cell action. This film is believed by Evans to have the property of allowing electrons to pass in one direction but prevents their passage in the other, thus making the film-covered area cathodic. He has been able to dissolve the iron and other metals away beneath cathode areas and leave a film of oxide. The value and accuracy of these researches cannot be doubted.

However, we should not lose sight of the fact that the energy relations of the concentration or solution cell are such that a current must pass through the metal from high to low oxygen concentrations and that this tendency would hold true even without the oxide film. The knowledge that in many practical cases including the corrosion of iron by aerated water this energy operates through the mechanism of an oxide film is most valuable in explaining the complicated course of the reaction. The presence and vital importance of these films should not be thought to be in antipathy or disagreement with the galvanic or solution cell. The cell concept is of the thermodynamic origin of the energy of the action. The film is part of a mechanism which allows the energy to produce results. Consider again, for instance, the anomalous position of the anode of the solution cell, that is, in the less corrosive solution. Without question the "one-way" film is most active in producing this result.

To return for a moment to the analogy of the sled on an icy incline, the *cell* is like the pull of *gravity* and the *film* like the runner and ice *contact*. The energy to cause action, *gravity*, may be there but unless the *contact* has suitable properties no effect is discernible.

Practical Application of Theory

As was stated above, this action of iron is a specific case of a quite general phenomenon. Whenever corrosion takes place, the corroding film changes chemically, tending toward exhaustion of the corroding constituent, at the point where corrosion starts. Any solid or colloidal product of corrosion concentrates and tends to prevent the replenishing of the corroding medium. In neighboring areas, where for any reason the corrosion has been less active, the corroding medium has better access to the metal, and the differences in concentration in the contact film set up an electric cell, with the protected portion the anode and that open to corroding solution the cathode. Any point over which the amount of solid corrosion product begins to concentrate thus becomes anodic and becomes more so as corrosion pro-

ceeds. The amount of corrosion depends upon the supply of corroding agent to the *cathodic* areas, but most of the metal disintegration occurs at the *anodic* areas, which thus become pits. The action of the current is in the direction described because the corroding reaction must be such as to furnish plus charges to the metal, and the areas over which a greater concentration of available plus charges are present are cathodic whereas those over which lesser concentrations are present must be anodic.

In practical work there are many cases of electrolytic corrosion where it is impossible to say "This is a two-metal galvanic cell" or "This is a solution or concentration cell." Their action often takes place simultaneously and inseparably. On the other hand there are many cases where the corrosion is obviously due to one class or the other. Where a pipe line carries a corroding solution at a high rate of speed sweeping off all corrosion products and keeping the liquid film in contact with the metal at uniform concentration and the pipe line is made of metals of widely differing corrodibilities there will be ordinary two-metal galvanic corrosion at the joints. Where a metal tank lining is of the same *homogeneous* material and the liquid quiet and corrosion products form on the surface of the metal there will be concentration or solution cell corrosion in pits or local areas on the metal lining. If corrosive solution stands quiet in the pipe line the concentration of corroding agent and corrosion product in the film of contact will change and be different at different points and there will be a combination of two-metal and solution cell corrosion.

DEZINCIFICATION

This term is used to mean the corroding away of one constituent of any alloy leaving the others more or less *in situ*. This phenomenon is perhaps most common in brasses containing high percentages of zinc but the same or parallel phenomena are familiar in the corrosion of aluminum bronzes and other alloys of metals of widely different chemical affinities. It is interesting from its very striking and destructive effects. It is an illustration of the two types of concentration cell corrosion and their interaction with galvanic cells.

It usually becomes evident as an area with well-defined boundaries and within which the more noble metal becomes concentrated as compared with the original alloy. In the case of brass the zinc is often almost completely removed and copper is present almost in a pure state, but in a very weak mechanical condition. Corrosion by the formation of such areas is usually quite rapid and since the corrosion is much localized it is one of the most destructive forms of corrosion. The most favorable conditions for dezincification seem to be a good conducting solution, as salt water, and a slightly acid condition with the presence of oxygen.

The mechanism is probably as follows. Due to any accidental variation in the corroding solution or the metal a concentration cell or a galvanic cell is formed and one area of surface is corroded more rapidly than a neighboring one. The more highly corroded area thus has over it a concentration of copper in solution greater than that over the other area, forming a metal-ion concentration cell which deposits the copper nearly at the spot where it originally dissolved. The original concentration cell continues to act, being accelerated by the formation of insoluble corrosion products. Some copper remains in solution and the copper-ion cell thus is retrieved and acts continuously adding its effect to that of the original cell to dissolve more metal at the anodic area under the corrosion product and the copper mass. The copper mass acts as a cathode in a galvanic cell which operates in the same direction. As corrosion proceeds the solution in the copper mass becomes acid enough by anodic action to keep the zinc in solution and allow it to migrate under the effect of the current out to the edge of the mass where it is carried away or precipitated due to the lowered acidity in the body of the corroding solution.

CORROSION-CRACKING-FATIGUE

Damage to metal from exposure to cyclic, or fatigue, stresses may be intensified very markedly by exposure at the same time to a corrosive atmosphere or solution. In cyclic stresses of the nature of simple repeated bend and of a rotating beam, it is the surface layers of the metal that are most highly stressed. Corrosion likewise involves the surface layers first. The damage known as corrosion fatigue results from both influences.

Two factors in the progress of corrosion fatigue damage are well to keep in mind. One is that corrosion of the surface of metal lowers its fatigue resistance. The other is that fatigue stresses accelerate corrosive action. Consequently metal corroded will be found to have subsequently a lower fatigue limit than uncorroded, and therefore even greater damage results where corrosion and fatigue are at once present.

Corrosion in the absence of cyclic stresses is normally superficial and confined to the surface of the metal itself. Corrosion simultaneous with fatigue stresses leads to pronounced penetration as evidenced by cracks, with the result that the damage due to corrosion fatigue may be—and often is—great.

The fatigue or endurance test is ordinarily carried out in air. It has been shown by Gough and Sopwith⁴ and by Beckinsale² that, strictly, such a test should be considered as corrosion fatigue, since fatigue limits in a partial vacuum or with the exclusion of air are higher than the normal air fatigue limits. Nevertheless, air in general is less damaging than aerated salt water.

The evidence suggests that oxygen is the exceptional damaging agent in corrosion fatigue of lead. Lead was found to be damaged far more when tested in air than when tested with a protective film of oil or in an acetic acid bath.⁵ In the acetic acid dissolved oxygen was used up in depolarizing hydrogen and so was kept from entering the metal.

What seems to be further evidence that oxygen is necessary is that copper has had higher fatigue resistance when tested in water than when tested in air, and highest of all when tested *in vacuo*. The fairly heavy corrosion product developing in the water tests is believed to have been an obstacle to the ingress of oxygen.

Deep, steep-walled cracks are a characteristic of corrosion fatigue. Presumably the part corrosion must play in producing corrosion fatigue is to start such a crack or at least to set up a condition where such a crack can be started by the fatigue stresses. Corrosion exposure of unstressed metal is much less likely to lead to premature failure than in the case of stressed metal. It is believed that the stressing damages the film of corrosion product, oxide or otherwise, and lays bare the metal to more or less unrestrained local corrosion. If the film can be conceived as being cracked open in places by the stress, then corrosion may progress at these cracks. The metal at these cracks, being less readily accessible to oxygen, probably becomes anodic to the surrounding metal and consequently is subject to accelerated corrosion. This view of the course of premature fatigue failure fits in well with the well-known fact of the importance of the film in normal exposure.

Corrosion Cracking. The term "corrosion cracking" is used to include failures of a different nature from those known as corrosion fatigue failures. Whereas the latter result from simultaneous corrosion and fatigue stresses, failures of a corrosion cracking nature derive from simultaneous corrosion and static stresses. These static stresses ordinarily exist in metal from the strain of cold work. Cold-worked, high-zinc, brass, for instance, will crack more or less spontaneously in an environment that might not be damaging to annealed brass. Cold-worked Monel metal has been known to crack—handling mercury or mercury salt solutions—where annealed metal has been satisfactory.

Corrosion that produces cracking of this nature is intergranular. The damaging medium must have a high penetrating capacity. Penetration, leading undoubtedly to some chemical action on the intergranular material, destroys the tenacity and releases the internal strains. The spontaneous disintegration results.

The intergranular attack of 18-8 or of duralumin is not strictly corrosion cracking. Stress is not a necessary accompaniment. Improper heat treatment will produce an intergranular phase that is susceptible in the absence of strains to attack.

FORMS OF CORROSION

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Chapter III

Corrosives

In classifying corrosives one possible method is to use the *chemical* composition of the major constituent which has been done in the several tabulations of corrosive effect popular a few years ago. Another is to group them more generally according to their *physical* nature as atmospheric, liquid, etc., which has been used in organizing American Society for Testing Materials work. We take the liberty of crossing these lines rather ruthlessly and group the common conditions without direct regard to their chemistry or physics but according to their analogy in corrosion reactions. This grouping is thus illogical chemically, for instance, but is useful in rationalizing corrosion.

CORROSION BY AIR

The atmosphere as opposed to solutions is practically continuous. Its composition, therefore, does not vary as much or as definitely as that of solutions or soils. However, it does vary in certain of the constituents which affect its corrosive properties, so that corrosion rates in one atmosphere may be several times that in another.

The corrosive constituents which exist almost universally in all atmospheres are: water, oxygen and carbon dioxide. The oxygen content is large compared to the amount actually taking part in corrosion and is practically constant. Carbon dioxide is not present in such large amounts and varies to some extent with climates and conditions. Moisture is the most variable constituent, changing from such low humidities in dry climates as to hardly support corrosion at all through the especially destructive humidities near the dew point to a high excess of rain and fog.

Any corrosive material which gets into the atmosphere may add its bit to the effect of these major constituents and if more corrosive it may often account for the greater part of the corrosion. As a matter of fact much of our corrosion in settled areas is due to two other constituents, chlorine and sulfur compounds. These with the major constituents above mentioned complete the list which needs our attention, except for special cases of atmospheric pollution.

The chlorine compounds originate mainly in sea water and are principally concentrated and active in narrow belts along salt water. Their action decreases rapidly in the first half mile from the shore and is usually unimportant at distances greater than five or ten miles inland. This condition, however, varies considerably with climate, wind velocity and direction.

The sulfur compounds, coming mainly from modern fuels, are more prevalent and active than any other constituent although, of course, it is not logical to compare them with moisture and oxygen because in most atmospheric corrosion the three can almost be compared to the links of chain: if one is missing the other two are of little effect. The sulfur compounds seem to drift farther from their source and to be in general more active in atmospheric corrosion than the chlorides although in solution the reverse is true. In sea coast cities the analysis of corrosion products shows a predominance of sulfates over chlorides and only in shore locations exceptionally free from drift from towns or factories are the chlorides in excess.

The presence of solid or liquid particles in the air, which may or may not consist mainly of chlorides and sulfates is productive of corrosion. Such particles form points for the collection of moisture and other active corrosives and a means of transferring them to a metal surface. They aid in fog formation. When settled on the metal, they produce small concentration cells which hasten corrosion and they may set up galvanic cells if of suitable composition and conductivity.

The effect of films both of the thin protective variety and the heavier corrosion product deposit, which in the atmosphere usually causes acceleration, is probably more varied and positive in the atmosphere than in any other corrosions.

The lack of solvent and physical washing action favors the building up of protective films and of corrosion products. A surface which is corroding in the atmosphere usually shows these films and much can be learned about the corrosion from them. Apparently most metals can form protective films of a sort in the atmosphere and practically all corrosion products will remain where they form unless removed by gravity, mechanically or by rain or high humidity and fog drip.

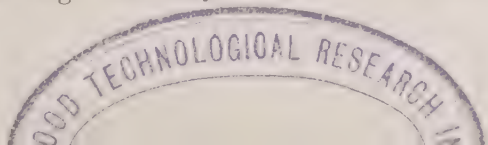
Many of the solids which deposit on metals and most of their corrosion products have the property of absorbing moisture at humidities less than 100 per cent. Thus it is often the case that deposits of corrosion products or foreign material on metal surfaces will be manifestly wet when there is no visible moisture in the air. (A knowledge of whether this is due to adsorption, gel action, or chemical affinity, would clarify our views and so help combat corrosion, but for a general understanding we must omit discussion of such undecided points.) The rate of corrosion of the surface increases rapidly at some humidity, probably closely related to this mois-

ture manifestation, and corrosion rates are much higher at relative humidities above such values than below. These humidities vary in rather wide limits with the metal and the corrosion product. They are, for instance, near 100 per cent for many copper corrosion products,^{16, 46, 47} around 85 per cent for certain nickel products, and possibly 65 per cent for iron. Corrosion may proceed at a destructive rate above these figures whereas a drop of a few per cent will reduce it to practically nothing. Thus, the amount of corrosion may be a direct function of the time humidities are in a certain range—one metal may be better within this range while its rival is better below it. The relative humidity is thus a determining factor in atmospheric corrosion rates.

Air movement is of importance from several angles; moving air brings uniformity of conditions more rapidly than quiet air. Humidity is usually higher at night. In windy weather, it drops promptly with rise in temperature and wind rapidly dries any deposited moisture. In quiet weather relative humidity remains high, when dew has been deposited, near heavy vegetation, or other sources of moisture. Thus wind may tend to shorten the high humidity corrosion period.

On the other hand some air movement is necessary to supply moisture, oxygen and other corrosives to the surface of the metal and, therefore, wind of high enough humidity and particularly if carrying chlorides, sulfates, or other non-gases, will increase the rate of corrosion.

Air drift and wind distribute our greatest corrosive, sulfur compounds. Metals exposed to wind-drift from high fuel-consuming areas will always corrode more rapidly than those not exposed to this drift. The sulfur compounds may change their nature and, therefore, their type of action as carried by the wind. Ordinarily, the sulfur compounds are in a "reduced" state when driven into the air. Common forms are hydrogen sulfide and sulfur dioxide. These are gases at ordinary temperature and may diffuse and travel like the other gases of the air. They are very readily absorbed by contact with any solid surface possibly by an action combining chemical reaction (oxidation) and solution in surface moisture. They may be easily detected quantitatively in the atmosphere of cities.²⁸ If these gases—in the low concentrations in which they exist come into contact with buildings, ground, or vegetation, they are rapidly removed by adsorption, so they are mainly found within a few miles of their source. If they remain in the air without contact with solids, they are oxidized to sulfuric acid which is then present in water solution as a liquid either adsorbed on dust particles or as independent microscopic drops. In either form their ability to make contact with and adhere to metal surfaces is obviously dependent on certain conditions of contact. Without attempting to explain the intricacies of these, it is obvious that high humidity and a certain amount of air move-



ment is favorable for their action. Corrosion products both in sulfur dioxide atmospheres and sulfuric acid atmospheres are sulfates of the metals.

Wind blowing over sea waves drives droplets of spray into the air. Those which are small enough are carried along and become smaller by evaporation. This produces microscopic particles of dry sea salt or drops of salt-saturated water which may exist at fairly low humidities and be carried some distance before settling out or being adsorbed. These particles are visible on any bright, brisk day at sea as a haze, denser near the water, which is probably the source of much seashore corrosion. Where humidities are not exceptionally low, this saturated solution will gather in films on metal surfaces in dull and even in bright weather if the surfaces are not directly warmed by sunlight. If it dries in place, a film of salt is left which is ready to absorb moisture from clear air and renew its corrosive effect at its "critical" humidity.

CORROSION IN SOILS

Soils are usually classified according to their origin and their composition differs through wide limits according to the origin. As is the case with fertility, the property for which soils are studied most, the total analysis of the soil is a most imperfect guide to their corrosive action. In fact, there is an interesting parallelism between corrosion and plant growth in that both depend on certain minor constituents, or rather certain minor forms of the total constituents which are quite difficult to segregate and measure. Further than this certain of the minor constituents which largely affect plant and bacterial growth—for instance, acidity, oxidizing agents, temperature, texture, and moisture content—also affect the rate and extent of corrosion.

The soil corrosion studies of the National Bureau of Standards ^{20, 21, 22, 23} have shown that the rate of corrosion changes rather distinctly from one soil origin class to another. These studies ⁷ have also shown a relation between corrosion, soil acidity, texture and drainage. While the acid concentrations of soils are small compared to those met in chemical and industrial practice, the acid varies largely in percentage of its own concentration, being such as to furnish hydrogen-ion concentrations changing from those so low as almost to inhibit corrosion to those high enough to support it readily. Acid concentrations are often high in wet marshy soils, low or neutral in loose well-drained soils. Alkaline concentrations of considerable extent may exist in dry soils. Soluble salts may increase corrosion, particularly localized corrosion, by raising the conductivity of the corroding medium and allowing current to pass freely. Some salts may also enter into the corrosion reactions. Thus the presence of salts in themselves tends to increase corrosion. However, the conditions which cause high salt concentrations in soils also produce low acidity and increase alkalinity. The practi-

cal result is that the accelerating effect of high salt concentration is usually more than offset by the absence of acids.

The temperature probably affects corrosion in the usual way by causing it to increase with a rise of temperature. But the temperature also so affects the other factors that this direct result may be largely obscured by its secondary effects through other factors.

A certain moisture content is necessary to destructive corrosion. Very dry soils have low corrosion rates. Hygroscopic moisture held above the water level in contact with metal and soil particles is liable to have a high concentration of acid or other corrosive constituents. However, unless there is sufficient movement or change in this moisture to furnish a supply of corroders, the corrosive constituents may become exhausted and the corrosion stop.

Up to a certain point corrosion will increase with increase in moisture due to the greater tendency for concentration or solution cell action as moisture films become thicker around soil particles. If the moisture continues to increase beyond a certain point, the concentration of corrosives lessens, the specific resistance increases and further increase has a smaller effect. If there is enough water to restrict oxygen penetration in the soil, corrosion may decrease.

If moisture increases to the extent that it is practically continuous and fills the air spaces, the supply of corroders is liable to be sufficient to make corrosion proceed steadily in the more acid soils where this condition ordinarily exists. If the water line or "table" is well above the corroding surface it will shut off the supply of air, conditions are reducing and the amount of corrosion will depend mainly on the acidity or secondarily on sulfur compounds and any specific corrosives which may be present. Under these conditions pitting will be less pronounced.

Oxygen from the air penetrates soils to an extent depending on their texture and moisture content. Oxygen takes part very largely in the growth of vegetation and bacteria and its concentration and amount in the soil depends largely on the result of this participation. The net effect of plant growth is the production of oxygen but part of the reactions of growth are oxygen consuming. Where growth is abundant dead vegetation is usually rotting in the soil and the rotting uses oxygen. Damp soils, therefore, with much vegetation will contain little or no oxygen at considerable depth and this will tend to lower corrosion rates. Loose soils will contain oxygen and are able to support the types of corrosion in which it takes part.

Decay also produces the reduced sulfur compounds, such as hydrogen sulfide and sulfur dioxide, which are active in corrosion. These gases are also a constituent of natural gases and oils and may be present in quantity from this source.

The reactions of oxygen as affected by the contacts of soil particles and soil moisture on corroding surfaces is a clarifying example of the operation of concentration cells.

From the concentration or solution cell concept we would expect pits "where any solid . . . can remain as a film or mass in close proximity to the metal."²⁷ In the case of soils "Corrosion is caused by oxygen concentration cells which are set up as a result of the partial or complete exclusion of oxygen at the points of contact of metal and soil. Soil particle size influences the rate of corrosion by determining the extent of the electrode areas and therefore the degree of cathodic polarization of these oxygen concentration cells."³ ". . . the greater the permeability of the soil, exclusive of sands, the greater is the tendency for corrosion to be confined to pits, other conditions being the same."⁷ Three-way contact between the metal, the soil particle or mass and a film of moisture with air in contact with the moisture sets up an ideal concentration or solution cell. The neighborhood of the particle-metal contact becomes a corroded anode because it is fairly well screened from oxygen and the small amount which may be there is removed by reaction with the metal; the moisture film carries enough dissolved salt and acid to be a fair electrolyte; it is supplied with sufficient oxygen from the air spaces in permeable soil to produce a strong cathodic reaction at a short but distinct distance from the anode and local corrosion proceeds nicely. The rate of pitting in soils is greater as particle size increases until the number of cathodes or the moisture supply become too small, as in sands.

Concentration or solution cells also act in soil corrosion of pipe lines on a larger scale. These are caused by the contact of the line with soils of different character. The extent of the anodic and cathodic areas is determined by the distance the line travels in each class of soil. Distances involved may be measured in feet or in miles. Several amperes of current have been measured and voltages of one-half volt are not uncommon.⁴⁰ Corrosion may be accelerated in exceptional cases in a few deep pits; usually it will occur in a soil of low electrical resistance as an anodic area considerably smaller than the cathodic areas.

The complicated combination of effects produced by variations in composition and texture, the fact that materials may be in contact with gases, liquids, and solids, during corrosion, and the variations of organic, inorganic and plant chemistry involved, conspire to make soil corrosion one of the most difficult types to analyze and predict. The students, therefore, who have managed to find such general principles as the increase of corrosion with acidity and of pitting with air contact, are to be particularly congratulated. The National Bureau of Standards corrosion tests have so clearly outlined the corrosive effects of various soils and identified the cor-

rosion with the soil characteristics that it is found possible in many cases to predict corrosive effects. Measurements of soil acidity, electrical resistance, permeability and moisture content are found useful in such predictions, and work now in progress should make these studies more positive in their results than they are at present.

CORROSION BY ACIDS

Corrosion by acids should, as stated in Chapter I, be considered in connection with other corrosives as well as independently. The fundamentals of the process have been described and in this chapter we consider the acid corrosion processes more specifically. For convenience the acids are grouped according to the type of their reactions in corrosion processes. Thus grouped they are:

1. Strong Acids,
2. Weak Acids,
3. Oxidizing Acids.

Sulfuric and hydrochloric are the strong acids which are not oxidizing.

These acids will actively attack many metals with direct replacement of hydrogen gas. Where this happens the rate of corrosion is usually so rapid that the metal is not practical as a container for the acid. A knowledge of the course this reaction will take enables a better understanding of the other conditions of corrosion.

The speed of this reaction tends to be proportional to the hydrogen-ion concentration, that is, to the "strength" of the acid. Acetic acid is a weaker acid than hydrochloric and therefore it corrodes metal by this particular mechanism less rapidly. The action is accelerated by rise in temperature.

The evolution of hydrogen physically affects the reaction in several ways. There is resistance to the process due to reluctance of the hydrogen to appear as gas. This is a property of the metal to a certain extent but also depends on specific conditions of the surface. It is often called overvoltage. Overvoltage may also exist due to the formation of other corrosion products but the term as usually applied refers to overvoltage of hydrogen.

Once hydrogen appears as a gas, being a non-conductor of current and being bulky with respect to the reacting materials, it offers a resistance to the reaction by preventing the flow of current and thus interfering with contact between the corrosive and the metal. This effect (usually considered principally from the angle of current conduction) is called polarization. The surfaces may also be polarized by other corrosion products but hydrogen is the most general offender.

There is a tendency for pure metals to react more slowly with acids at first contact than they do after the reaction has been proceeding for some

time. This tendency may be so exaggerated that upon first contact the metal practically does not react at all. If this condition exists for a considerable period of time, and it often does, it is called passivity. It has been explained on the basis of homogeneity of the metal surface preventing the necessary formation of galvanic cells, and on the basis of the formation of thin solid oxide films, and as a peculiar atomic condition due to partial reaction with oxygen. The acid reaction is often combined in corrosion with others making up a complex which progresses gradually.

The most common combination of reactions is that of acid replacement and oxidation. This may be typified by the reaction between acid, air, and copper which causes the corrosion of copper by acid solutions. It is as follows:



Note that three distinct forces are at work: (a) the tendency for copper to oxidize (increase in valence); (b) the acid reaction between hydrochloric acid and copper; (c) the union of hydrogen and oxygen to form water. (b) and (c) will not proceed by themselves at room temperatures and (a) will proceed only very slowly. But since all work in the same direction, they pull together and the combination proceeds so rapidly as to produce destructive corrosion.

Some attention has been given to the separation of such reactions into parts. If copper reacts with the acid first liberating hydrogen which then unites with the oxygen, we might expect certain results which would be changed if copper reacts with the oxygen first and the copper oxide then reacts with acid. In the writers' opinion, the same practical effects are predicted whether the reaction is considered as a unit or in steps; and since we can measure the reaction as a whole but not in parts, the practical student of corrosion may make his problems simpler by considering the reaction as a whole.

In this typical reaction the gas oxygen may be replaced by many other oxidizing agents. But oxygen gas is probably the most common of the oxidizing agents which take part in this reaction. In the practical handling of acids by metals, a reaction of the above type is often taking place slowly against some resistance of its own generation or some other combination of circumstances. Therefore, the conditions surrounding it are of great significance.

The conditions which retard and accelerate this reaction are in some respects the same as those affecting the simple acid reaction. Its rate tends to be proportional to the hydrogen-ion concentration, and it increases in rate with rise in temperature. The physical effects of hydrogen gas polarization and overvoltage, as they exist in the simple acid reaction are pre-

vented by the oxygen. The part which oxygen plays is independently increased by increase in concentration and temperature.

There are other simple but vital facts to be considered in regard to the oxygen. Its best condition for simultaneous contact with acid and metal is in the dissolved state but oxygen is only sparingly soluble in most corroding solutions. This means that a small amount of corrosive action will seriously depreciate the supply of oxygen at the points where the reaction proceeds. A continued replenishment of the supply is necessary if corrosion is to continue.

The oxides of the metals are very often non-conductors of electricity and insoluble in water so that their presence or absence may have a vital effect on corrosion rates. Many of the protective films which are valuable factors in preventing corrosion are oxides of the corroding metal or alloy or oxides modified by some minor constituent.

The acid which is produced and used in the greatest quantities is sulfuric. It is a strong acid and corrodes most metals rapidly in the presence of air or other oxidizing agents. The standard metal for handling sulfuric acid is lead. In contact with acid lead forms a coating, probably a mixture of lead oxide and lead sulfate, which is highly insoluble and which prevents further corrosion by preventing direct access of the acid to the metal. The exact composition of this film may vary under different conditions. If the acid in contact with the lead is in rapid motion from the instant of first contact, these corrosion products may be removed as fast as formed and then the lead corrodes at an appreciable rate dependent on the acidity, oxygen concentration, temperature, and supply of corrosive reagents. If motion stops for any appreciable interval of time the protective coating forms and the corrosion rate becomes much lower and is not economically destructive.

Aside from its manufacture, sulfuric acid is also widely handled in lead and in the many cases where lead is unsuitable on account of its physical properties, in nickel and copper alloys and in high silicon cast iron. In the case of the nickel and copper alloys the presence of protective films is relatively less important than with lead. Concentrated sulfuric, due to its low ionization and low solubility for oxygen gas can be handled with impunity in cast iron and even in wrought iron and steel.

In the wide variety of uses of sulfuric acid in industry where structural strength and lightness are requisites, various alloys are used and their suitability depends largely on the amount of dissolved oxygen present in solution and its supply to the contact film. The supply to the surface is, of course, dependent on the rate of movement. Rise in temperature increases the rate of corrosion but its effects are probably not as serious as that of oxygen

solubility. Most of the alloys are free from attack if the sulfuric is air free and most of them are corroded so rapidly as to be uneconomical for use if the acid is thoroughly saturated with air and in rapid movement.

The soluble corrosion products as well as the oxygen in solution tends to set up localized corrosion by concentration cells where the rate of movement varies on a surface, at crevices and at air-water lines. Corrosion products are relatively bulky and easily visible when insoluble. They probably tend rather to increase corrosion than to be protective except in the case of lead.

Hydrochloric acid is on the whole more active than sulfuric acid and this trait is reflected in its corrosive properties. The true reason for this difference has never been clearly explained. Certain contributing factors are: the greater solubility of chlorides, less tendency to form insoluble basic salts, and higher mobility of the chloride ion. Hydrochloric acid also has a strong "peptizing" effect, or property of producing charged mobile particles from material (protective oxide) otherwise insoluble. This property causes rapid corrosion in places where with sulfuric acid the metal would be rather fully protected. In the manufacture of the acid its activity is so great that little metal can be used, the equipment being stone or pottery.

Hydrochloric acid in the concentrations used in industry is also often handled in high silicon cast irons and in copper and nickel alloys. However, it is chemically so active that this is not always practical, and the development of a truly resistant common alloy would allow the use of the acid in places where it is now impractical because of corrosion. Its action is even more affected than that of sulfuric by the presence of dissolved oxygen and by high temperature. As a result there are many conditions in which it cannot be handled in any metal. Very dilute acid and very strong acid may be handled without too great difficulty if at reasonably low temperatures and not too much oxygen is present. Intermediate strengths are usually unsatisfactory in metal. Corrosion by hydrochloric acid is more likely to set up concentration cells and pitting than that by sulfuric acid and its course and rate is more erratic and difficult to predict.

Phosphoric and acetic acids are generally less active than sulfuric and hydrochloric but rank with them in the rate of corrosion on most metals. Both are strongly affected by the presence of dissolved air. Corrosion by acetic acid is often accompanied by the formation of protective or semi-protective films so that large variations in rate are present under different conditions on the same metal. Since acetic acid in most of its uses is required in a high degree of purity, its handling in metals must be done with consideration for this fact. In the absence of air the acid itself will attack the metals relatively less so that metals may be used. In the distillation of the acid air is usually absent and this may be done in metals.

Pure phosphoric acid is relatively active but can be handled in several different alloys. However, most of the phosphoric acid of commerce contains an appreciable percentage of ferric salts. These salts are highly corrosive and where they are present they present a combination of oxidizing agent and acid which is destructive.

In the weaker acids are grouped the ordinary fruit acids and organic acids. Unless inhibited by the presence of colloidal or other interference, corrosion by all but the very weakest of these may be very rapid (See Organic Materials and Foods). This is because in most cases of acid corrosion the resistance to action is mainly due to lack of an oxidizing agent or to some outside interference, rather than to a dearth of hydrogen ion. Very weak acids furnish a sufficient hydrogen-ion concentration to produce rapid corrosion if an oxidizer is present and the path is otherwise clear. Due to the conditions of occurrence of these acids, however, as in foods and soils, the contact conditions and the lack of oxygen hold the actual damage done by them to smaller proportions.

In the oxidizing acids, nitric, perchloric, nitrous, etc. the necessary oxidizing agent is always present with the hydrogen ion. It is therefore practically impossible to use metals in contact with the oxidizing acids except in a rather limited minority of cases where conditions allow a continuous protective film to exist. The number of such cases has been much increased during recent years by the advent of the chromium iron alloys.

The more stable of these acids, as nitric, perchloric, and chromic allow the existence of the protective film to be more positive than the less highly oxidizing, but less stable ones such as nitrous, hypochlorous, and sulfurous. The latter offer a free path for the corrosion process and their rapid action is often quite striking when compared with that of the former. The salts of these acids when present in an acid solution produce rapid corrosion, of course, just as though the corresponding acid had been added.

OXIDIZING AGENTS

The subject of oxidizing agents as corrosives closely parallels the subject of oxidizing agents as rate factors discussed above (Chap. I, p. 20). This discussion, from the standpoint of the commonly existing oxidizing corrosives, should clarify and expand their consideration purely as a rate factor.

The tendency to combine with oxygen is present in most metals and varies widely with different metals. It is very weak in such "noble" metals as gold and platinum, and strong with iron and aluminum. There are many conditions which interfere with direct oxidation and practical corrosion problems deal very largely with the type of such interference.

Most metal oxides are difficultly soluble and they are often poor electrical conductors. Under certain conditions they may form a valve, checking the flow of current in one direction and allowing it to pass in the other.¹⁰ The resulting tendency to form "passive" or "cathodic" films in oxidizing corrosion forms one of the major problems of corrosion now under theoretical investigation.

Unless the oxidizing agent acts in a solution which, by its acidity or otherwise, has the ability to dissolve the oxide or other compound formed, the corrosion does not continue. If the oxidizing agent is an active one, and the resulting metal oxide or other compound is readily dissolved, corrosion is rapid. It follows, therefore, that a solution with the correct proportions of oxidizing material to acid is one of high corrosive properties. This is the reason that materials like nitric acid, and ferric salts, are extremely corrosive. On the other hand, in such strong oxidizing agents as chromates, concentrated nitric acid, the oxidizing power is so great as compared to the acidity that the passive oxide film forms and corrosion is inhibited. Evans,¹⁰ as above, corroborated and modified by other workers,^{31, 45, 14} has actually demonstrated the presence of insoluble oxide films in many cases where metals are passive in corrosive solutions. These films are so thin as to be invisible, but Evans believes them to be of much the same nature as films produced on iron by heating in air.

Whatever the inherent mechanism, it is important to bear in mind that the most rapid corrosion takes place with a properly balanced high concentration of acid and oxidizing agent. The balance cannot be expressed numerically as it depends on too complicated a series of inherent properties of metals, acids and oxidizing agents. With chromium iron alloys for instance, mixtures of nitric and hydrochloric acid can be made up so that a slight addition of either will change the corrosion rate by several hundred per cent (see chart, p. 22), and this change can be repeated up or down the scale depending on whether the oxidizing or non-oxidizing acid is added. With copper-nickel alloys, on the other hand, the balance is so undelicate that small changes have relatively little effect.

In stainless steels as compared with copper-nickel alloys and considering sulfuric acid as the acid, and dissolved oxygen as the oxidizing agent, the maximum ratio of oxidizing agent to acid for the stainless steels is probably not 1/100 of the value of the copper-nickel alloys. A state may easily be reached and often exists practically in the common acids and oxidizing agents on chromium-iron alloys, where this oxide formation practically stops the corrosion reaction.

The most commonly distributed oxidizing corrosive agent is atmospheric air dissolved in water. A very large majority of cases of corrosion would be very much ameliorated were atmospheric air excluded and many cor-

rosions would entirely cease. Some air is present in almost all plant corrosive conditions and laboratory corrosion tests. When present it is an active controlling agent and in the majority of cases it is the most active agent. No analysis of a plant corrosive condition can be correct without consideration of the effect of air or its absence, and no laboratory tests conclusive without an intimate knowledge of air conditions or a thorough means of removing air. A few illustrations follow. The ordinary corrosion or rusting of iron would cease under most conditions if air were excluded. The corrosion of copper and nickel alloys more noble than hydrogen, such as Monel metal, of bronzes, and of acid-resisting brass by strong mineral acids such as sulfuric and hydrochloric, which these metals are commonly used to handle, would entirely cease without the presence of air; other oxidizing agents will cause corrosion here but are ordinarily absent in industrial practice. In the acid pickling of steel where corrosion proceeds at the enormous rate of 1,000,000 mg. per sq. dm. per day with rapid evolution of hydrogen, an efficient air-saturating device speeds up the reaction rate from 10 to 20 per cent. Some chromium-iron alloys will remain permanently in contact with acids in contact with air but are corroded rapidly by the same acids if air is excluded.

The air content of corroding solutions is not easy to determine. The known methods of analysis are difficult of manipulation and inaccurate in inexperienced hands. Therefore it is expedient to be able to estimate with some definiteness the main factors in connection with the presence of air in corroding solutions. A fundamental point in such estimation is the very dilute solutions possible under ordinary atmospheric conditions. While air is a relatively strong oxidizing agent, its action is often so slow as to be unnoticeable because of its low solubility in water. At ordinary temperatures oxygen is practically inactive unless dissolved, and the strength of a saturated solution at 70° F. is less than 1/1000 of 1 per cent and at 140° F. only half of that strength.

Another matter for consideration is the rate at which air may enter or leave water. Figures from which practical conclusions may be drawn on this point are not available, but as compared to the rate at which air may be removed at a corroding metal surface, the rate at which it may be replenished at a solution-air surface is quite small. In an ordinary metal tank open to the air containing an unagitated solution which corrodes it the air content may only be a few per cent of saturation except right at the water-line. Fresh solution drawn into the tank may be air saturated or not depending on whether it is handled in corroding piping and whether it is churned up with air in pumping or pouring into the tank. Water handled in such closed systems as household heating plants and power boilers will be partially free from air due to corrosion, and the air admitted in solution will

be rapidly exhausted by corrosion and the amount of corrosion will be largely proportional to the air which is admitted.

Solutions contained in wooden tanks may often be air saturated, particularly if handled for long periods in contact with air or through centrifugal pumps with air leaks or poured from one level to another in such a way as to carry bubbles of air underneath the surface. Air saturation by mechanical means is rather a slow process and requires an efficient device for breaking up the air stream into small bubbles and distributing them through the solution.

Obviously the low concentrations of air which can exist mean that rate of supply of air to the corroding surface is quite dependent on some movement. It is a known fact that in cases where the corrosion is governed largely by the air content as in steam condensers, rapid movement causes unusual acceleration.

The presence of some common impurities in small amounts may affect the air content. Many organic compounds such as foods, fats, and sugars will react with dissolved oxygen removing it from solution. Dyeing and bleaching materials are often oxidizing or reducing. Many forms of bacteria "breathe" oxygen thus removing it.

Another widely distributed and important oxidizing agent is iron in solution. Soluble iron compounds exist easily in an oxidized or reduced state depending on their contact with the air. One-thousandth per cent of iron in water gives an oxidizing capacity several times that due to the solubility of air and such water is corrosive practically in proportion. Other oxidizing agents will of course produce the same effect but iron salts are most common. In corroding metals these salts tend to produce soluble metal salts rather than oxides and therefore do not form protective films as readily as some other oxidizing agents. However, while iron salts will often increase the corrosion of a wide range of corrosion-resisting alloys they are, with the chloride rather an exception, protective to stainless steels and some bronzes. Being easily hydrolyzed iron salts produce acid solutions and this faculty increases their corrosive effect tremendously.

The corrosion of any iron structure may produce soluble iron salts, and the general use of iron in construction increases the distribution of this corrosive agent. A typical example of this is the corrosive nature of mine waters. Iron is usually present in solution in such waters and their acidity is often due to hydrolysis of the iron salt. Such waters are very corrosive and this destructive action is typical of the combined action of acid and oxidized iron solution.

Copper salts have the same facility as those of iron for existing in the oxidized or reduced state. In proportion to their distribution they are just as corrosive. They have less tendency to produce protective films and in

addition to their direct effect they may precipitate by contact on many metals. The precipitation is a form of corrosion and the copper deposit increases corrosion galvanically. Silver and other noble metals often act as oxidizing agents being easily reduced to metallic form from solution. Like copper they tend to accelerate the corrosion of many metals galvanically, and are therefore dangerous corrosive agents. They are only protective when deposited in an impervious coating.

The ordinary run of oxidizing salts among which may be listed nitrates, chromates, chlorates, permanganates form neutral solutions when dissolved in water. They are not particularly corrosive in these neutral solutions, but if present in connection with acids may be very active. Since they tend to produce oxides they readily cover the metal with protective oxide films and therefore probably act as inhibitors more often than accelerators.

Solutions of the halogen gases, chlorine, iodine, fluorine, bromine, are extremely active corroding agents in acid solution, often in neutral, and sometimes in alkaline solution. Chlorine in slightly alkaline solution is widely used as a bleaching agent and is quite corrosive. Because the oxidizing action of these gases produces soluble salts their protective effect is very slight. Other bleaching agents such as hydrogen peroxide and sodium peroxide are oxidizing and therefore actively corrosive.

It should be noted that the "strength" of the oxidizing agents is not a criterion of their oxidizing effect. Chromates are stronger oxidizing agents than iron salts, that is chromates will oxidize iron salts, but the latter cause more rapid corrosion. In the same way the nitrates are in a higher state of oxidation than nitrites but the nitrites are much more corrosive. The criterion is a rather vague or at least unmeasured property which may be designated as "ease" of reduction or decomposition. Oxidizing agents of a relatively unstable type are the most destructive as corrosives.

NATURAL WATERS

The corrosive effects of natural waters are largely affected by their appreciable content of other materials than water, absorbed by their contact with rocks and soil. Sea water may be considered an average concentrate of natural waters, but from a corrosion standpoint its high concentration causes action so different from other natural waters that it will be mainly considered under the chemical salts and brines.

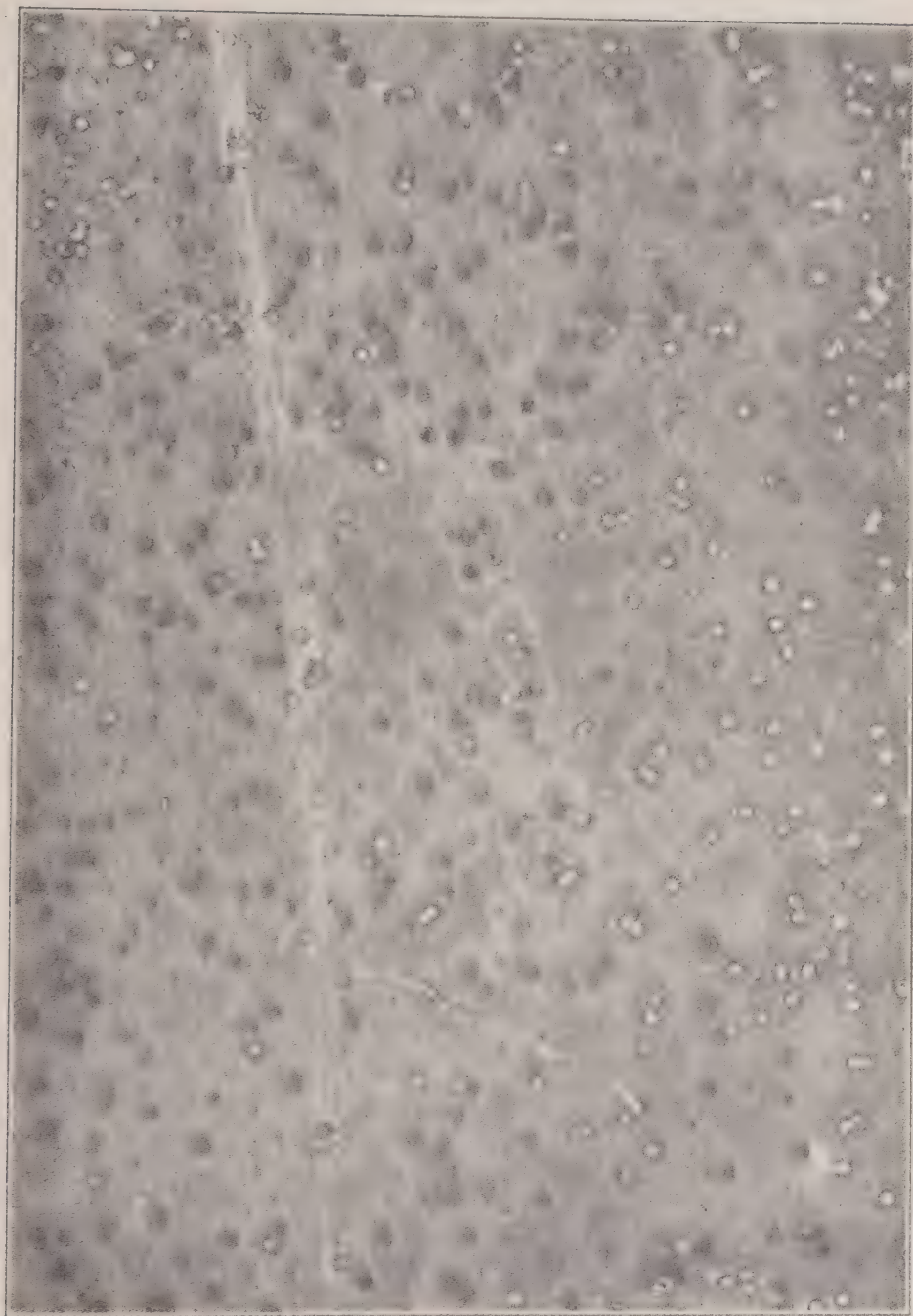
Natural waters other than sea water may be very different from each other, both in the quantity and kind of foreign material they carry, depending upon the kinds of earths with which they have been in contact and the length of time they have been in contact. They may be acid or alkaline in reaction, may contain oxidizing or reducing agents, and their electrical conductivity may vary in a wide range.



Section Across Pitted Tube. $\times 33$.

PITTING CORROSION

This solution cell pit was probably started by some adhering matter and continued due to the presence of tightly packed, but porous products of the continuing corrosion. Perforation occurred in about 18 months.



Distribution of Pits over Sheet Surface. Natural Size.

PITTING CORROSION

The commercially homogeneous surface of this alloy sheet was pitted due to slight surface inequalities or floating particles from the solution. Pitting continued due to the adhering corrosion product.

With so much variation in these rate factors variation in corrosive effect is to be expected. In the case of the corrosion of iron and probably other metals, the variation in ability to form protective films is large and the effect of these films may be a controlling factor above all the others.

The corrosive action of water varies principally with its acid content,² its air content,^{2, 50, 48} and its ability to form films.

The decomposition of animal and vegetable matter produces acids which although weak in hydrogen-ion concentration may be very destructive in corrosion. Waters which have been in contact with these acids as they exist in soils ordinarily known as "acid" soils, will have a high acid content and will corrode by their acid reaction.

Waters which have been in contact with dry soils, low in acid, are liable to be alkaline in reaction and from this standpoint will not be corrosive. However, these dry soils may give up salts and oxidizing agents in some cases which are corrosive.

The oxygen of water is one of its most variable corrosive contents. Water which has been underground for long periods, particularly if it has been in contact with metallic or carbonaceous reducing agents, may be quite free from oxygen. Surface water in running streams and shallow ponds may carry oxygen up to saturation. Deep lakes and the ocean contain considerable oxygen at the surface and little or none at depth. Water confined in metal pipes, particularly iron pipes, loses its oxygen rapidly by corrosion and thus loses its corrosive power. These naturally occurring variations in oxygen content will often change the corrosion rate by several hundred per cent and under laboratory control may change it by 1000 per cent. While the oxygen content is not usually determined in water analysis, a knowledge of its amount is essential to a knowledge of the corrosive effect.

The surface of metals immersed in natural waters is liable to become covered by a film or protective condition which slows down corrosion tremendously. In fact it is probable that if the surface of iron, aluminum, possibly nickel and many other metals were kept free from such a film their life would be very much shorter than is commonly experienced. The nature of this film or condition has been given considerable study during recent years and some of the laws governing its formation and preservation are becoming known. The investigations aimed directly at measuring the composition and physical properties of the film have been somewhat inconclusive. Probably the best opinion on this matter visualizes the film as an oxide of the metal existing in so thin a sheet as to be unweighable and transparent to light. It is possible that research into these questions is too far from the practical or tangible for discussion in this work. Oxide films without weight or color are not things of common experience.

On the other hand, some of the conditions under which metals become passive in waters have been determined together with corrosion rates in the passive active and intermediate states. Waldron and Groesbeck, as quoted above, and in as yet unpublished work, for instance, have been able to duplicate in the laboratory the seasonal variation of corrosion of Washington city water and identify it with specimen surface conditions. This is done by manipulation of the oxygen and calcium carbonate contents of the water. Their results seem to explain certain practical features of natural water corrosion which have caused much speculation in the past.

These findings are in good agreement with the action which would be expected from the general considerations discussed under "Acids" and "Oxidizing Agents," and well illustrates the two opposite effects of oxygen. Where sufficient acid is present the corrosion rate increases with the oxygen supply to the surface. Thus it increases with the dissolved oxygen content of the solution, and with the velocity of movement. However, under many conditions the air supply can be too large relatively for the acid content and when this happens the corrosion rate diminishes as the oxygen increases, apparently because the surface becomes passive. This action may be due to the formation of a protective film and it may be considered as a form of the reaction of oxygen which produces and maintains the cathodic areas of concentration cells. The cathodic effect here exists to the exclusion of the anodic effect and thus inhibits corrosion.

In the case of iron in natural water the presence of a practically saturated solution of calcium carbonate aids in the protection of the metal. In water with high calcium carbonate content oxygen produces passivity with much greater ease than when the calcium carbonate is low. Therefore in the case of iron at least, and probably other metals, calcium carbonate has a protective effect modified by the relative concentrations of oxygen and acid. This effect is again chemically logical. The reaction of oxygen with metal in corrosion removes acid from solution, in this case carbonic acid. This removal precipitates calcium carbonate which is less soluble when the acid is removed. This precipitation at the metal surface forms a basic carbonate film protecting against corrosion. The recent work mentioned shows the practical importance of this action in governing corrosion in Washington water and due to the natural prevalence of a saturated condition with respect to calcium carbonate the findings must be widely applicable.

Natural waters are also much in contact with silicates of various types. Certain silicates inhibit corrosion and are used commercially for this property. Since the solubility characteristics of silicates are not as clear as of calcium carbonate it is not possible to formulate their action with positiveness. However, it seems obvious that in waters saturated with silicates these

compounds have an important part in the natural protection of metals from corrosion.

"Reduced" sulfur compounds, particularly hydrogen sulfide, are often present in waters coming from deep in the earth. As described elsewhere these compounds are very corrosive and their presence in water is usually quite destructive to metals. Their effect is quite variable and is related to the oxygen supply. Waters from great depth from which the oxygen has been thoroughly removed may contain high sulfur and be corrosive by their acid reaction entirely. As these waters reach the surface and are supplied with oxygen the forms of corrosion change entirely and the rates usually increase.

While it may be considered that natural waters are mild corrosives in comparison with concentrated acids, brines, etc. it is to be expected from the wide variation in its contained materials, both which cause corrosion and which protect against it, that the corrosion problems in connection with such waters are relatively complicated.

CHEMICAL SALTS AND BRINES

Each chemical salt or brine is a separate corrosion problem and the reactions which take place are dependent on the salt and the metal concerned. In considering such specific corrosions it is well to realize that each case has these individual characteristics. It is only possible here to discuss certain useful generalizations.

Following the general rule for chemical reactions water is usually necessary for corrosion to proceed. Thus *perfectly* dry salts are practically non-corrosive at ordinary temperatures. Ordinarily commercial dry salts are not very corrosive and their action is multiplied many times in the presence of appreciable moisture.

Certain salts in their water solutions will produce corrosion according to characteristics discussed elsewhere, namely, acid, oxidizing agent, active sulfur compounds, or alkali. Salts which are oxidizing agents or which contain the active sulfur compounds should be considered under these heads. Many salts hydrolyze when dissolved to give an acid or alkaline reaction and their corrosive action is then typical of the acid or alkali concerned.

Concentrated salt solutions are good electrical conductors as a rule and this has an important bearing on their corrosive effect. Good electrical conductance encourages electrolytic corrosion by galvanic and concentration cell action and such corrosion may be expected if there is any tendency toward it due to the presence of different metals or variations of concentration due to the shape of the apparatus or other cause.

The solubility of corrosion products is an important factor in corrosion because the presence of insoluble corrosion products reduces the ability of

the corrosive to make continuous contact with the metal. Some salts are so constituted as to produce mainly insoluble reaction products with the metals and with others the products are largely soluble. The chlorides, bromides, and fluorides (halides) are quite soluble and tend to be corrosive. Metal compounds of the silicates and carbonates are insoluble and these salts are less corrosive than the halides. Ammonium compounds tend to form soluble double salts with the metals and therefore are quite corrosive.

Such a general rule must be subject to many exceptions due to special conditions. For instance, the tendency for the formation of insoluble products is often a tendency to produce passive or cathodic areas which, if anodic or active areas continue to exist, cause destructive local electrolytic corrosion. For this reason mild corrosive conditions are often accompanied to a greater extent by local corrosion than more drastic ones.

The most widely occurring salt is sodium chloride or "common salt." The corrosion reactions of this salt are illustrative of chemical salts which do not have such specific corrosive properties, as for instance, an acid reaction. The salt does not hydrolize to produce acid or alkali and it does not contain oxidizing agents or sulfur. On the other hand it has the properties which tend to produce corrosion by chemical salts. It is highly soluble in water and since most chlorides and salts of sodium are also soluble it tends to produce soluble corrosion products. It is a good conductor of electricity and is therefore favorable for the formation of galvanic and concentration cells.

Sodium chloride does not ordinarily react direct with the commercial metals, but due to its favorable electrolytic and solubility properties even traces of materials which can set up a reaction will produce serious corrosion in salt solution. With metals of high solution pressure such as aluminum and zinc, reactions may go forward with nothing else present but salt and water.

All the ordinary rate factors have strong effects on corrosion by salt solution. The presence of a slight amount of acidity and of oxygen in solution will cause rapid action on metals otherwise practically immune to salt. Increase in temperature increases corrosion. Galvanic effects are very severe and the starting of a concentration cell pit produces rapid corrosion where there has been none before. The passive effect of films is very positive, and film-forming inhibitors will often stop corrosion. Movement has its maximum effect both in furnishing corrosive to the surface and distributing inhibitors and dispersing concentration cells.

Sodium sulfate solution, having a lower conductivity and forming metal sulfates of generally lower solubility than the chloridēs, is less corrosive and less acutely susceptible to the rate factors. Calcium chloride has lower conductivity and the calcium salts are less soluble. At the same hydrogen-ion

concentration and oxygen content calcium chloride is less corrosive, but due to hydrolysis of calcium chloride to form acid and to the greater solubility of oxygen in calcium chloride solution, calcium chloride refrigerating brines are often more corrosive than sodium chloride brines.

Sea water is a special case of salt corrosion and so many tests have been made on it and so much unrelated experience built up that the writers hesitate to generalize on it. Sea water produces a large amount of corrosion and most of this occurs in harbors. The waters of harbors are more variable in constitution than the open sea and, as a rule, more corrosive. The natural corrosiveness of sea water is increased in harbors by corrosive impurities, acids, oxidizing agents, sulfur-bearing organic materials, etc. The natural dilution of harbor waters also produces an unsaturated condition with respect to calcium carbonate and any other film-forming constituents and thus prevents the formation of protective films.

Corrosion by sea water is complicated by the presence of animal and vegetable life. Surface sea water is usually saturated with oxygen. Oxygen is used by marine growths and the oxygen disappears at depths which vary with currents and the amount of growth.

Many marine growths adhere to metal and other objects and set up direct action or concentration cells by their presence. A barnacle attached to a metal surface is a complete concentration cell and its interior free from any corrosives that act directly on the metal, particularly dissolved oxygen, and with its shell forming a conducting screen to keep this anode producing solution separated from the cathodic solution outside. The exact outline of a barnacle may often be seen accurately etched into a metal surface and barnacles may start pits which penetrate deeply.

The corrosion of marine and shore steam condenser tubes is a serious sea water corrosion problem, this being one of very few cases where an unprotected metal is used in actual sea water contact. The corrosion of condenser tubes is obviously greater in harbor waters than on the high seas, is greater at high temperatures and velocities than low and is obviously susceptible to galvanic and concentration cell effects and the presence of dissolved oxygen. Turbulence of motion at the inlet end will produce very rapid corrosion, particularly so if much dissolved air is present. Any slight defect in the tube surface is a potential anode and while condenser tubes may pit without defects, their presence is usually fatal.

These generalities illustrate the many sides of corrosion by the chemical salts. It seems impractical to attempt detailed analysis of the many reactions involved. However, there is evidence in the illustrations that certain general laws are applicable.

ORGANIC COMPOUNDS AND FOOD PRODUCTS

Organic compounds as a class are not active corrosives. They do not ionize in their water solutions to produce acids and are not oxidizing agents. They are usually non-conductors of electricity.

Compounds containing sulfur or chlorides may react directly with metals to cause corrosion but the general run of oils, alcohols, paraffins and benzenes are relatively non-corrosive.

Dyeing solutions are often corrosive but this activity is usually due to inorganic acids or oxidizers used in conjunction with the actual dye compounds. Many dyes change shade with the slightest content of metal salts, being even more sensitive than foods to metal contamination. Thus the corrosion problems in dye plants need careful solution, but they involve analysis of the common acids and chemicals present rather than the dyes themselves.

The petroleum industry, likewise offers many complex corrosion problems, largely connected with inorganic compounds. Only at high temperatures do the oils themselves react destructively.

Food products range from the weakly alkaline solution of many cooked vegetables and meats to a definitely acid condition in many fruits and in sour milk. Some foods contain weakly active sulfur compounds and most of them are reducing rather than oxidizing in their reactions. In the storage of foods low temperatures and freedom from oxygen are desirable and these conditions are favorable for the prevention of corrosion.

In considering corrosion by foods a contrary angle of attack to that ordinarily made is necessary. The question is not one of deterioration of the metal but rather of the effect of the metal on the foods. While this angle needs consideration in the handling of many chemicals, waters, and dyestuffs, it is of paramount importance in the case of foods. In most cases this means a different order of magnitude in the allowable corrosion rate from the limits for metal deterioration. An amount of corrosion almost undetectable and at least unimportant in metal deterioration is often so high as to be ruinous to a delicate food. For instance, minute amounts of iron will largely affect the color of cherries and wines and a small amount of zinc will change the flavor of milk.

Much has been written and said on the harmful effects of metals in foods on the health of consumers. This is not a subject to be passed over lightly. However, in certain cases the dangers of metals in foods have been exaggerated, possibly for commercial reasons. Aside from certain known poisonous compounds which contain metals, foods will be so changed in appearance or flavor as to be unpalatable before the metal content reaches an unwholesome amount. Some metals are a usual and necessary constituent of foods.

In the preparation of foods by boiling or steaming, conditions are normally weakly alkaline or acid and the oxygen supply is low. While the corrosion rate will be small it is necessary that there be practically no corrosion in most cases. If handled in closed containers without access of air there is so little tendency for corrosion that metals are suitable which would corrode otherwise, but even in vacuum pans corrosive conditions are more severe in the atmosphere than below the solution level. These mildly corrosive conditions tend to encourage pitting of metals in long service. Pitting is not permissible because of the danger of deterioration of food being held in the pits. To prevent pitting, properly selected metal without defects is necessary.

When moist food is laid on tables, the area under the piece or mass is shielded from air while the edges of contact with the metal are well supplied with air. This condition is ideal for the propagation of oxygen concentration cells and is liable to produce corrosion in the shielded area, particularly close to but just inside of the air contact. The activity of the cells depends on the corrosiveness of the food and is at a maximum with acid fruits and minimum with neutral vegetables. The presence of salt and to a certain extent sugar increases the conductivity of the liquid present and thus produces more corrosion.

This type of attack on metals is common where moist drops or masses may be on a surface. The edge of such masses is cathodic and an area just inside of this cathodic area tends to be locally corroded. The effect is readily noted with drops of salt solution on metals. The presence of solid foods in the mass exaggerates the condition because the cellular solid prevents distribution of the oxygen while allowing the passage of electric current.

The frying of foods in grease is not a corrosive condition and little metal effect can be expected from this source.

Fruits as a whole as well as a few other foods contain sufficient acid to produce reaction with metals. The color and taste of fruits are due to delicate chemical compounds easily affected by metallic contamination. The common fruit acids, malic, tartaric, lactic, and citric and acetic seem roughly to be more corrosive than would be expected from their low hydrogen-ion concentration. Quite rapid attack may occur in some cases. As would be expected the action is much more rapid in the presence of air. Fortunately the corrosion which would obtain were the acid present by itself in the same concentration as in the fruits, is inhibited by other constituents. To attempt to explain this useful inhibition in detail would be guess work. However, in the case of milk, casein is known to exist in colloidal dispersion and when milk is heated in an ordinary dairy surface heater a palpable protective film is formed which is largely casein. It seems probable that any such colloidal dispersion would inhibit corrosion and that a slight electrical disturbance

such as occurs in corrosion might be expected to precipitate the colloid as a protective film.

Milk, a major food product, is one of the largest quantity liquids of commerce. Sweet milk is slightly acid with lactic acid and as it is handled in bulk in contact with air is often air saturated. In this condition it is rather corrosive to metals. Being very sensitive to contamination the allowable metal corrosion is very small and only metals proven to be free from action on milk can be used with it. In the manufacture of many dairy products milk is allowed to sour so that it contains one per cent or more of lactic acid. With air present this gives a combination of acid and oxidizing agent which will produce rapid action on all but the most resistant materials. When milk is being heated a protective coating tends to form on metals with which it is in contact, but this film does not form during the cooling process. Cheeses and other dairy products are corrosive in proportion to their acid and air content.

In the preservation of foods it is common practice to seal them in closed containers out of contact with air. While certain foods will cause corrosion and will deteriorate under such treatment a very large number can safely be sealed in metal cans for long periods. It has been common practice to use tin-coated steel cans for this purpose and during recent years the number of foods so stored has increased and their quality has improved. In some cases the metal cans are coated with appropriate lacquers.

The freedom from corrosion on the inside of cans is due to the complete absence of atmospheric oxygen and illustrates the inherent dependence of corrosion on oxygen. Another interesting point which aids in preventing destructive corrosion is that in the interior of cans in many foods the tin instead of being cathodic to iron as is the case in the atmosphere and in salt brine is anodic. Thus a slight perforation of the tin plate is sealed up and does not cause perforation of the can.

Certain foods among which may be mentioned clams and pineapples are corrosive to an extent not readily explainable by their chemical constitution.

HIGH-TEMPERATURE OXIDATION

Corrosion by atmospheres at high temperatures is a distinct phenomenon from that at ordinary temperatures. The mechanism is so different and so complicated as to make it rather a separate study and yet because of certain similarities and connections, it may be logically connected with our main subject. Possibly the fundamental difference is the absence of liquid water in the system. This is a particularly vital distinction since most other corrosion reactions are mainly dependent on water solutions of the corrosive agent. Another major quality of high temperature oxidation is the mobility of the reacting materials in gaseous and mobile solid solutions which serve

instead of water solution to produce the contact necessary for reaction. Reaction velocities are also much higher, so that the rates of actual oxidation are retarded by physical rather than chemical resistance.

The outstanding feature of high temperature oxidation is the effect of the film formed in controlling the course of further action. It is usually true that oxidation produces a film which is protective to a measurable extent. In the case of oxidation of several metals by relatively homogeneous atmospheres, the rate of attack diminishes with the time, the attack rate being proportional to the square root of the time. This is the relation to be expected were the reaction dependent upon the reactants making contact by diffusion through a separating medium^{1, 36} and is attributed to this cause. While it is natural to expect oxygen to be the reagent which diffuses, it has been shown at least in the case of iron, that the iron diffuses also and builds up scale on the outside of the existing surface^{11, 12, 13, 33} rather than oxidizing at the surface of the metal and forcing the pre-existing scale away. Where the process of scale or oxide film formation becomes complicated or non-uniform, the rate of oxidation varies and does not follow such a simple relationship with the time, but the rate continues to depend on the properties of the scale. If an alloy forms oxides which will react with each other or with one of the metals, the relations become complex. Complicated or changing atmospheres cause the same effect, and increase the rate of attack. In some cases where the scale formed is loose and porous the rate does not vary with the time but remains constant. Where the physical conditions of exposure are such as to damage or modify the scale as in furnace parts bearing mechanically on each other or being quenched periodically, no mathematical treatment of the scale protection problem is practical.

In some alloys scale formation is a complicated process, including diffusion of gases and metals both in the scale and in the metal itself. Therefore, in binary systems the rate:time relation is apt to be uniform near the ends of the system but in a central range the reactions become complex, the scale is not uniform and oxidation rates are uneven. This is true in air oxidation of copper-nickel³⁷ alloys and copper-zinc⁹ alloys. In the case of copper-zinc alloys the oxide coat is nearly free from copper on compositions containing less than 86 per cent copper. This must entail quite complicated diffusion processes resulting in retention of the copper in the parent metal. In alloy steel, analysis of the distinct scale layers which form^{33, 34} show segregation of metals which come from interaction between oxides of different metals with selective diffusion as well as from interchange of oxygen between oxides. The interacting oxides may be in contact but they can react through differing vapor pressures without solid contact.

In alloys of iron which have unusual resistance to oxidation, such as

alloys with chromium, nickel, and aluminum, the type of scale is very much modified and the actual rate does not follow mathematical laws.

As in corrosion at room temperatures the rate of attack increases with the temperature. This increase in typical cases may amount to doubling the rate in 167° F. This effect is modified by the effect of temperature on solidifying the scale. If higher temperatures consolidate the oxide making it less permeable the rate decreases. In most cases the scale will disintegrate by melting or vaporizing as the temperature is raised, causing an abrupt rise in oxidation rate. The type of scale may change at transformation points causing a break in the temperature-rate curve.

The concentration of the oxidizing or corroding agent at the active surface affects the rate in the same way as in low temperature corrosion. If the concentration is so low that the oxidation seriously depletes the atmospheric film in contact, increase in rate of movement of the atmosphere increases the attack.^{1, 30} Above a rate of movement sufficient to keep the concentration constant at the interface there is no further effect.

The constituents of the atmosphere have of course very great effects and these have not yet been reduced to reliable generalizations. It seems that oxygen, air, carbon dioxide and water vapor produce rates of somewhat the same order of magnitude, with the effect of water and oxygen possibly twice as great in a moderately high temperature range as air and carbon dioxide. Water is a catalyst for almost all reactions⁴⁴ and this seems to hold true in these cases. Oxidation by air, oxygen, carbon dioxide and sulfur dioxide is increased by the presence of water vapor.^{11, 12} On some metals certain proportions of carbon dioxide, steam and air act together to produce maximum effects.

Hydrogen sulfide and sulfur dioxide are most destructive constituents in many furnace atmospheres. Under oxidizing conditions hydrogen sulfide will oxidize rapidly to sulfur dioxide. The action of these gases is most rapid when present under such conditions, that is with other sources of oxygen present. However, they can react direct with many metals to form sulfides and another oxidizer is not necessary. Sulfur dioxide, for instance, will react completely with nickel to form nickel oxide and nickel sulfide. Metal sulfides in general have relatively low melting points and thus are not protective and may destroy the protective value of oxide films containing them. Possibly due to this fluidity sulfur tends to produce intergranular deterioration as well as surface attack, especially on metals under strain.^{29, 30, 34} By and large the combination of sulfur dioxide and water in the same atmosphere seems to be an exceptionally active condition in ordinary furnace atmospheres, and several other combinations are more destructive than either of the gases by themselves. Rates may change with these combinations as much as 10 to 1. It should be noted that in many

furnaces, gases do not reach equilibrium and that the resulting variable action on metals destroys the continuity of protective oxides and so increases the attack.

Hydrochloric acid which has been found in some atmospheres, can increase the normal oxidation rate by as much as sixty-five times. The result is mainly catalytic and would not be detected by examination of the oxide. While this gas may not be a common constituent of furnace gases, its startling effect indicates the value of thorough knowledge of the furnace atmosphere.

SULFUR COMPOUNDS

Sulfur with its compounds is to be ranked near to the all-pervading oxygen in its corrosive effects. Like oxygen, sulfur combines directly with the metals and with hydrogen. It might thus be classed with the other oxidizing agents but because it also acts chemically as a reducing agent, both as free sulfur and in many of its compounds and because of other chemical peculiarities it needs separate consideration.

Sulfur ranks with oxygen in chemical affinity for the metals. Many metals occur in nature as sulfides, and as with the oxides there is a constant tendency for them to return to the natural state. The metals alternate with a certain amount of regularity in their affinity for these two corrosive elements. However, uncombined sulfur at room temperatures does not react in corrosion to the same extent as oxygen, probably mainly because it is completely insoluble in water. In order for it to become active at these temperatures, it must be in a soluble form and it takes this form by combination with other elements.

In corrosion sulfur ordinarily appears as hydrogen sulfide, H_2S , or sulfur dioxide, SO_2 . SO_3 , the anhydride of sulfuric acid, also appears widely in corrosion but its action is like that of the other strong acids rather than the sulfur compounds, and it is considered in that section. In spite of the fact that H_2S , SO_2 and SO_3 represent three advancing stages of oxidation, the intermediate compound, SO_2 , is by far more active as a corrosive oxidizer than either of the others. This property of a partially oxidized or unsaturated oxidizing agent being more active in the oxidizing or cathodic part of the corrosion reaction is something of a general phenomenon and is worthy of consideration. Nitrous acid, for instance, is more corrosive than nitric and not as prone to produce passivity. Many other complicated sulfur compounds exist. They contain more sulfur or oxygen atoms and are to be classed roughly with H_2S and SO_2 as corrosives.

Sulfur dioxide, the common form of sulfur in the atmosphere, usually corrodes metals with the formation of sulfates. Sulfates are the largest constituent of atmospheric corrosion products after the oxides and hydroxides.

In water solution sulfur dioxide furnishes both sufficient acidity and oxidizing power to produce rapid corrosion on most metals. It will react with nascent hydrogen practically as readily as does oxygen with the production of water and hydrogen sulfide. At the same time the sulfurous acid formed by its combination with water liberates a considerable concentration of hydrogen ion. This gives it the necessary requisites as described under acids and oxidizing agents to produce corrosion. As contributing to the oxidizing part of the fundamental acid and oxidizing reaction of corrosion, sulfur dioxide is nearly as active as oxygen. Because it is many times more soluble than oxygen it can reach the metal surface in larger quantities and thus in many cases it is more destructive than oxygen.

Sulfur dioxide is used sufficiently in chemical industry, for instance, the paper industry, to make its corrosive properties in concentrated form a serious problem. However, probably it is most often met with as an impurity or small constituent in corrosive mixtures. Its presence in the atmosphere is usually high in the vicinity of towns and industrial plants where it is produced in the combustion of fuels. Its corrosive effects are evidenced by the obviously high corrosion rates on roofs bathed in smoke and in any place where smoke is cooled sufficiently so that moisture can condense. For instance, in scrubbing towers for cleaning the products of combustion, sulfur dioxide has been found to corrode destructively almost all of the common corrosion resisting alloys. The prevalence of sulfates, which are the major product of sulfur dioxide corrosion, in all atmospheric corrosion products in thickly settled areas is mentioned elsewhere.

Sulfur dioxide in small quantities is also often present in ground waters, particularly "mineral" springs. As a product of oxidation of hydrogen sulfide, it is often present in conjunction with hydrogen sulfide in the many places where this gas is found.

Hydrogen sulfide is present in many ground waters, including sea water. It is produced with allied compounds by bacterial action in the decomposition of vegetable and animal matter and is thus widely present in soils, air and water. While in water solution it is a weaker acid than sulfur dioxide, it is still sufficiently acid to produce corrosion on many metals. However, because it can only satisfy the cathodic or oxidizing requirements of the fundamental corrosion reaction weakly, if at all, it is not as corrosive as sulfur dioxide.

Hydrogen sulfide is often present in crude oil deposits and its occurrence and corrosive action in the drilling and refining of oil are illustrative of its properties. It is present at the bottom of oil wells as a by-product of the decomposition processes which produce the oil. While it exists in the presence of salt brines there is no oxygen or other oxidizing agent with it. In this condition it is corrosive to iron and other non-acid resistant alloys

whereas nickel and acid-resistant nickel alloys are relatively unattacked. When pumped to the surface it comes in contact with air and becomes very much more corrosive to the acid-resistant alloys. At the surface the order of usefulness of metals in resisting the corrosion is quite different from the order in the same waters at the bottom of the well. This is because the air has furnished such an excess of reagent for oxidation that the relatively weak acid condition is overshadowed. Sulfur dioxide is also gradually produced in contact with air furnishing a new corrosive constituent.

The oil itself, while still containing sulfur, is not corrosive at ordinary temperatures but when heated to cracking temperatures the sulfur reacts directly with metals and again does much damage. Hydrogen sulfide is present in swamps and places where decomposition occurs and is responsible for much of the corrosion in connection with them. Bacteria in lakes and the ocean produce sufficient hydrogen sulfide to aid in the corrosiveness of the water.

The distribution of sulfur is so wide that no corrosion problem should be considered answered unless it is definitely known whether or not it is present.

ALKALIES

In corrosion by alkalies one of the principal and most universal corroding factors is absent by definition. That is the hydrogen-ion concentration is low. In addition to this the hydroxides of the metals are often insoluble, particularly under oxidizing conditions. Thus the alkalies are not nearly as universally corrosive as the acids. Their corrosive effect is usually due to special or individual chemical affinities and is thus not as readily subject to generalization as acid corrosion.

Ordinarily the particular types of corrosion which occur readily in acid are stopped by the presence of alkali. For instance, the corrosion of iron in air-saturated solutions is relatively rapid when the solution is slightly acid. If alkali is added to such a solution it will usually stop the corrosion quite positively. Nickel is corroded at an appreciable, slow rate by hydrochloric acid. The gradual addition of caustic soda to such a corroding solution will slow down the corrosion through neutrality until, when definitely alkaline, the rate is a very small fraction of the original rate. The absolute rate both in acid and alkaline solution will depend on the amount of oxygen present.

The most common corrosion reaction of alkalies is the formation of complex compounds in which the metal corroded tends to go into the anion. Double salts, basic salts or double hydroxides may be formed. They are rather closely allied in type with sodium ferrate and sodium aluminate which are the products of corrosion of iron and aluminum corroded by caustic soda.

Thus iron and steel are usually corroded little or none by strong alkalis when relatively dilute. At elevated temperatures and high concentrations such as exist in parts of the machinery used in concentrating caustic solutions, there is relatively rapid corrosion with the formation of sodium ferate and evolution of hydrogen. In the case of aluminum which is resistant to many acids the presence of alkali increases the corrosion even at ordinary temperatures and in dilute solutions. The reaction is accomplished by the evolution of hydrogen and formation of the aluminate of the alkali which is readily soluble in the alkali. The tendency for the formation of this compound and its ready solubility is of course the reason for the corrosive action.

Some hydrates of copper are soluble in the solutions in which they are formed and such alkaline solutions will appreciably corrode copper. In the case of ammonia the highly soluble double hydroxide is formed and corrosion is relatively rapid. Double hydroxides of metals formed with ammonium hydroxides are quite common. As they are relatively soluble, ammonia is relatively quite a corrosive material although it is neither acid, strongly alkaline nor oxidizing in the usual sense. However, the formation of double compounds with metals and ammonia can take place without the presence of air or other oxidizing agent and corrosion can proceed in this way. Also in the presence of air, air enters into the corrosion reactions and accelerates them.

Corrosion by alkalis is often characterized by pitting and localized attack. This would seem to be explained by the tendency for alkalis to produce cathodic films and thus concentrate the attack on given areas. The size and shape of pits will, of course, depend on the relative magnitude of the film-forming tendency and the rate of anodic reaction. A high film-forming tendency will force the anodic corrosion into small areas and pits will be small and deep and will penetrate relatively rapidly.

Another undesirable phenomenon often connected with alkali corrosion is embrittlement by hydrogen. Hydrogen produced in caustic solution in a nascent state, either by electric current or by corrosion will penetrate along the grain boundaries and react chemically with oxides and sulfides to produce permanent embrittlement. This effect has been principally observed on iron in alkaline boiler water but is also prevalent in strong alkalis on other metals.

CORROSIVES

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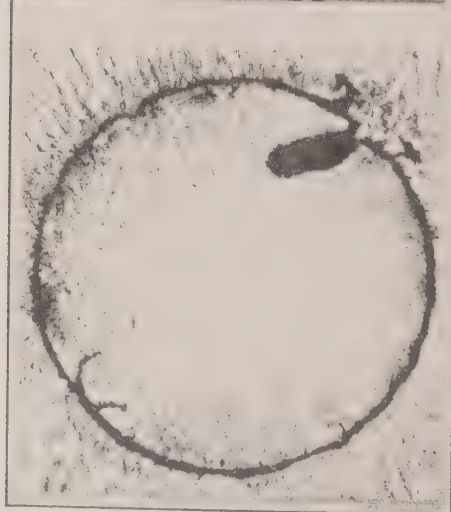
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A screen wire in which corrosion is caused by a seam fails completely while adjacent wires are relatively un-attacked.



Section through above corroded wire showing the defects which caused corrosion.

× 150

Chapter IV

Metal Corrosion Properties

The evaluation of the effect of Metal Corrosion Properties which are allied, according to Speller's ¹ able classification, to the "factors internal to the metal" is difficult at the present time. This is mainly because of a dearth of data which existed for some years and to the difficulty of harmonizing some apparently divergent results in the more voluminous contemporary literature. It may be said, with the greatest appreciation of the diligence and usefulness of their work, that the task is not less difficult because some writers have apparently not taken the time to look at their own results with sufficient skepticism. For the same reason references in this chapter are mainly listed by name only. It is difficult to definitely allocate the abstracted summary herein to the various able workers whose publications have helped form its basis.

CHEMICAL AFFINITY AND SOLUTION PRESSURE

Most commercial metals exist in nature in the combined state. Their ores or natural compounds must be subjected to certain furnace and chemical processes to bring them into the uncombined or metallic state. It thus follows that their natural tendency is to combine with other substances. This tendency of two materials to combine has been called chemical affinity and is measured in modern chemistry by the "decrease in free energy" of the system as the reaction proceeds.

This natural tendency of a metal to combine with other substances is an inherent or typical property of each solid metal and its strength varies from one metal to another. Metals like zinc and iron have a greater tendency to combine with other substances than do copper and silver. Some metals, called the "noble" metals are so low in this tendency that they exist in nature uncombined or combined so loosely that reduction to metal is very easy. Examples are platinum, gold and silver.

While this property is typical of the metal, it is also typical of the environment and the strength of the affinity (amount of free energy decrease) is a mutual property of the metal and the contact material with which it reacts. This means that the order, among metals, of the tendency

to be dissolved by a solution of hydrochloric acid is not necessarily like the order of the tendency in industrial atmosphere, the major corrosive of which is sulfur dioxide. Some of the metals will be rated in different positions in their order of tendency to corrode under the two conditions, but on the whole there will be a rough parallelism in the orders.

The actual *rate of corrosion* under such conditions will be very much more subject to variation than this *tendency to corrode*. This is due to the various considerations discussed under *rate* and *forms* of corrosion. The *tendency to corrode*, however, is present in all metals in varying degrees while the way it is manifested depends on the environment.

One of the phenomena of this tendency to corrode or chemical affinity is the solution pressure or solution potential of the metal. When in contact with a solution, for instance, the metal indicates its desire to react by a contact electrical potential. In many cases the relative value of this potential can be measured against a standard electrode, such as the hydrogen electrode. The actual potential determined relative to a standard electrode will depend on the metal and on the solution in which it is measured. By making such measurements of the (reversible) potential of a metal in a pure solution of its own salts which contains a standard concentration of the metal ions or by calculating to such a value in the many cases where experimental realization is impossible, the metals can be arranged in an *electrochemical* series in a more or less positive manner. Such a series can be considered a median or average guide to the tendency of metals to corrode and may be applied, when the proper complicated calculations are made, to other solutions also, but its values and the mathematics of applying corrections are not at present sufficiently accurate to predict without other data the practicability of particular corrosion-resisting uses. Thus, while this series of standard electrode potentials should be understood as of fundamental importance in corrosion, the mistake should not be made of drawing engineering conclusions as to specific corrosion-resisting properties of metals directly from it.

This chemical affinity of metals for other substances produces corrosion directly on a homogeneous metal surface in a homogeneous solution and if either is not homogeneous, local or electrolytic corrosion may result. If two metals, such as zinc and copper, under standard electrode potential conditions are electrically connected to each other and their solutions are also connected a momentary electrical potential will exist equal to the sum of their standard solution potentials. Zinc will corrode more rapidly than if unconnected and copper will be deposited on the copper electrode. If both copper and zinc are immersed in the same solution the potential will be in the same direction but will be different in value from that in the standard conditions. With metals close together in the standard series in the same

solution the direction of electrical pressure may be reversed from the standard so that the one lower in the series is corroded.

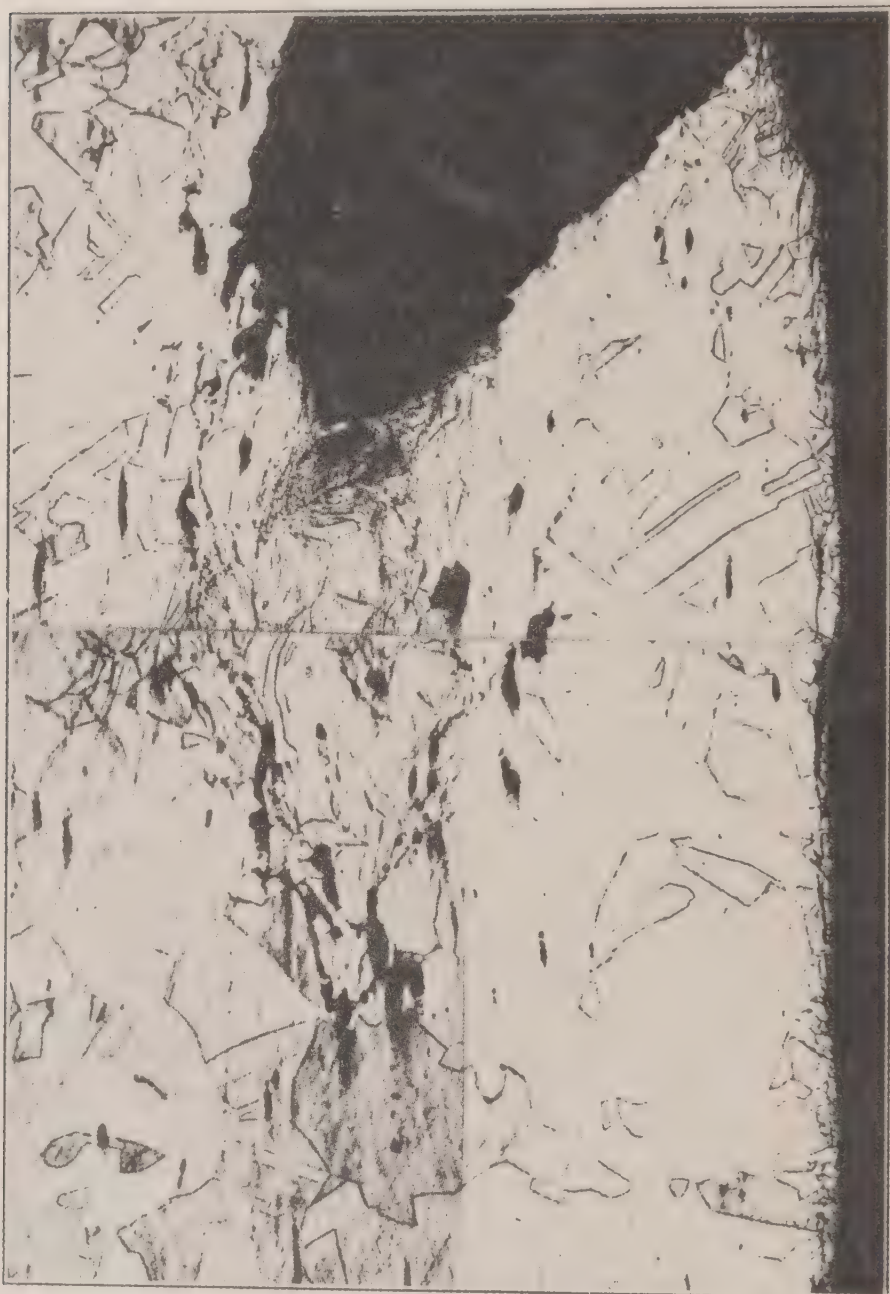
Thus, the electrolytic corrosion of metals depends not only upon their standard potential but also upon their affinity for the particular electrolyte in which they are immersed. It follows that if a homogeneous metal is held in contact with two solutions for which it has different affinities, electrolytic corrosion will result. Destructive corrosion with this variation in electrolytes as its major cause is very common, as in ordinary pitting.

In considering this fundamental tendency of metals to corrode we are dealing with energy relationships. This energy tendency in actual practice must operate through a mechanism which overcomes many obstacles to the progress of corrosion. These obstacles are at times so effective that they are of more moment than the fundamental tendencies in determining the course of corrosion. They are largely film contact phenomena such as oxide and salt precipitation, concentration change during reaction and inter-diffusion of corrosion product and corrosive.

OXIDATION PASSIVITY

Possibly the most generally pervading retardant to the direct action of the energy tending to produce corrosion is the tendency for the oxidizing part of the reaction to build up a resistance which prevents corrosion. This resistance, while partly dependent on certain environments, is exhibited to an extent which is a property of the particular metal in question. Attention has been centered on it by the development of the corrosion-resistant chromium alloys. Chromium, while it has a much higher combining affinity than, for instance, silver will retain an unchanged metallic surface *in an oxidizing environment* much longer than silver. On the other hand, in an acid environment, in the absence of oxidizers, silver is unaffected and chromium is rapidly decomposed. This oxidation passivity exhibited by chromium is present in all metals and is more prevalent in those with higher standard potentials. It is however, less uniform in its manifestations than chemical affinity. Certain metals such as chromium and aluminum possess it to a degree not predictable by their other chemical relations, and in some metals it is exhibited to a much smaller extent than would be expected by analogy.

This passivity seems to be a physical resistance and many researches have been carried on and mechanisms proposed to explain it. The obvious connection between its existence in oxygen-bearing solutions and the chemical stability, low solubility, and low electrical conductivity of metal oxides make the presence of an oxide film the most reasonable explanation. The minute detail of formation and properties of such a film are of the greatest interest, for in it lies the explanation of much practical resistance to cor-



DEFECT PITTING

The pit at top of photograph is following a region of porosity and inclusions. This is a section from a condenser tube operating in sea water.

× 100

rosion. On the other hand, the experimental difficulties of corroboration of the theories are a serious deterrent to positive conclusions. It is known positively that protective oxide films do exist in some cases. The difficulty lies in those more numerous cases where the film is presumably so protective that its thickness is too small to determine. Some investigators believe it may be something between adsorbed oxygen and an actual chemically combined oxide.

Oxidation passivity has an interesting analogy or connection with the cathodic depolarization of electrolytic cells. In the operation of these cells (see Chapter II) the presence of an oxidizing agent at the cathode is an active accelerator of corrosion at the anode. Thus, while the oxidizing agent accelerates the total corrosion, the actual solution of the metal is induced at a point less concentrated in oxidizing agent. In other words, the area in contact with the oxidizing agent is passive. On metals with sufficient tendency to oxidation passivity the whole area becomes cathodic or passive and in spite of a high tendency toward corrosion the tendency toward the oxidizing or cathodic part of corrosion prevents any action. As a natural consequence of this effect any anodic area which does form on metals protected by oxidation passivity corrodes at a higher rate due to its proximity to large purely cathodic areas. Since the prevention of this anodic attack is desired much study has been given to films formed on anodes with impressed e.m.f.

Again there is a certain relationship between this passivity and the inability of certain strong oxidizing agents to produce corrosion as rapidly as analogous weaker oxidizing agents. The resistance of iron and nickel to strong nitric acid solutions is an outstanding case of oxidation passivity and this property is lost in weaker solutions and especially in nitrous acid, which has less actual oxidizing energy.

The numerous cases in which protective oxide, and in some cases other composition, films exist have been reviewed by Hedges. He shows proof of the presence of economically protective films on aluminum, chromium iron and in some instances copper, including some of the alloys of aluminum and the stainless steels. In addition to the actual isolation of films by Evans, he quotes many laboratory experiments of his own and others which give direct and indirect evidence of the existence and properties of these films. W. J. Müller, in a number of papers has discussed "anodic" passivity. His data agree with those of Hedges, but he explains the mechanism differently. Dr. Sven Brennert has published a complete research on the formation of black spots on tin in which he postulates passive films as vital to the action.

In spite of the experimental difficulties involved, rapid progress is now being made in the understanding of this most vital property of metal electrodes. The writers believe that this progress will be even more rapid as

the complementary properties of the film cell and of the solution cell are better understood.

CORROSION PRODUCT PROPERTIES

Insofar as the properties of corrosion products are typical of the metal, the metal is responsible for the progress of corrosion. The corrosion products are produced at the point of corrosion and their tendency to diffuse or to be carried away, to prevent or encourage contact of the corrosive with the metal, to conduct or to resist electricity and to act as selective membranes for the passage of ions or electrons is most vital. Possibly the most obviously effective property is the solubility of these products. It is perhaps unfair for other reasons to compare the corrodibility of sodium and potassium on the one hand, having their range of highly soluble compounds, with the resistance of silver and lead which have low solubility in most compounds and many insoluble salts. But this relation also holds in many other cases where the effects are less exaggerated.

Corrosion rates of a reacting substance on a metal would be high beyond usefulness except for the resistance set up by the reaction layer. Pure reaction itself is infinitely rapid, but at any instant only a surface of metal and a surface of corrodent are free to react. The reaction taking place within the instant exhausts the available metal surface and the available reactant. A fresh supply of reactant must find its way to the fresh surface of metal before further action can take place, and this can take place only by diffusion through the reaction layer. The products of the initial corrosion must diffuse out from the metal and fresh solution in towards the metal.

The products of corrosion enter as a factor in setting up a resistance to this diffusion. The initial corrosion may have led to the formation of a solid, as frequently happens. Lead sulfate in sulfuric acid or chromic oxide in an oxidizing solution are examples. With these, diffusion is suppressed, the solid offering a serious obstacle, and the corrosion rate will correspond in the purest case to the solubility of the solid corrosion product.

On the other hand, the corrosion product may be a soluble salt, like copper chloride. The initial reaction leads to a solution layer that is highly concentrated in copper chloride and free of the reactant. There must be diffusion within this layer before corrosion can continue. In a case of this sort the equilibrium corrosion rate obviously will be much more rapid than where a solid layer intervenes.

Again, hydrogen gas may be a corrosion product. If the gas clings to the metal in a blanket—as with tin in air-free acid—further corrosion must await the removal of the gas by diffusion, which is extremely slow because of the low solubility of hydrogen. If instead of tin the metal is iron, then

the hydrogen will not cling to the metal but will evolve mechanically. In a case of this sort corrosion is rapid, since the evolving gas aids diffusion.

Corrosion rates therefore, come to depend on the nature of the diffusion layer, particularly in respect to corrosion products.

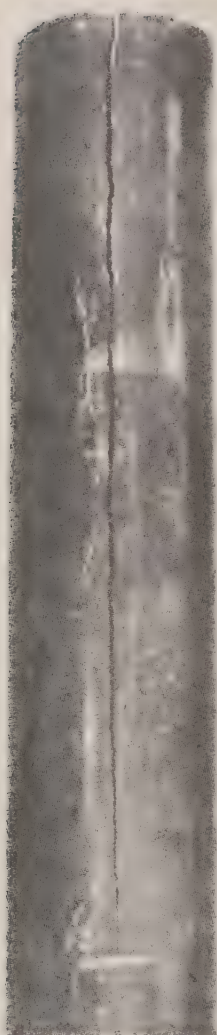
Most metals acquire an oxide layer in ordinary atmospheric exposure. Aluminum is a particularly good example, since it is only the persistence of the oxide that gives it useful resistance. This is true likewise of chromium alloys. Zinc and lead acquire similar protective coats and iron also, though less protective. Copper and nickel are superficially oxidized in the same way, not to mention other metals. The mechanism of these effects is considered under "Oxidation Passivity."

Iron offers a good illustration of the dependency of corrosion rates on the products of corrosion. In neutral solutions ferrous hydroxide is the important corrosion product because, being sufficiently soluble to be present in appreciable quantities, it maintains control over the reaction layer. If the solution is made basic the solubility of ferrous hydroxide is lowered and in consequence attack becomes correspondingly less. On the other hand, as the solution becomes more acid the solubility of the hydroxide becomes greater until finally it no longer offers an important obstacle to the replenishment of fresh solution at the metal surface, and the acid is free to attack at will. At this point, the corrosion product offers a minimum resistance, since the salt that is the principal corrosion product in the acid is highly soluble and hydrogen evolution aids replenishment of fresh solution. Yet, with iron in sulfuric acid, ferrous sulfate becomes decreasingly soluble as the acid becomes more concentrated, to the point that in high concentrations the salt precipitates out and protects the metal to make its use commercial.

The corrosion products forming on copper alloys in sea water steam-condenser tube service are an excellent example of the control these products may exert over corrosion rates. Varieties of products develop on such tubes, including oxides, hydroxides, oxychlorides, various salts in various degrees of hydration. Corrosion rates vary from virtually zero to about 1000 mg. per sq. dm. per day. If certain products form, corrosion is slight, if these do not form corrosion is rapid. The complexity of reactions and products is such that what goes on is only very vaguely understood.

In the atmosphere, as stated elsewhere, the attack of metals is very largely dependent on corrosion products. These build up more heavily than in submerged corrosion and action proceeds only to the extent that fresh corroder penetrates the products.

In high temperature gases the suppressing effect of the product is evident in its pure form. Corrosion rates often vary exactly as the square root of the time—the pure protective film effect.



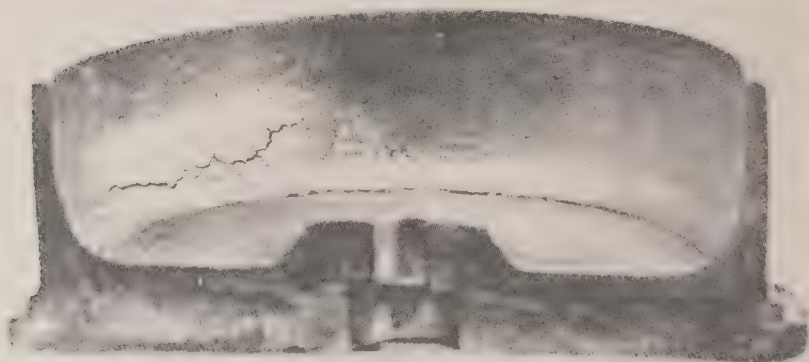
CORROSION CRACKING

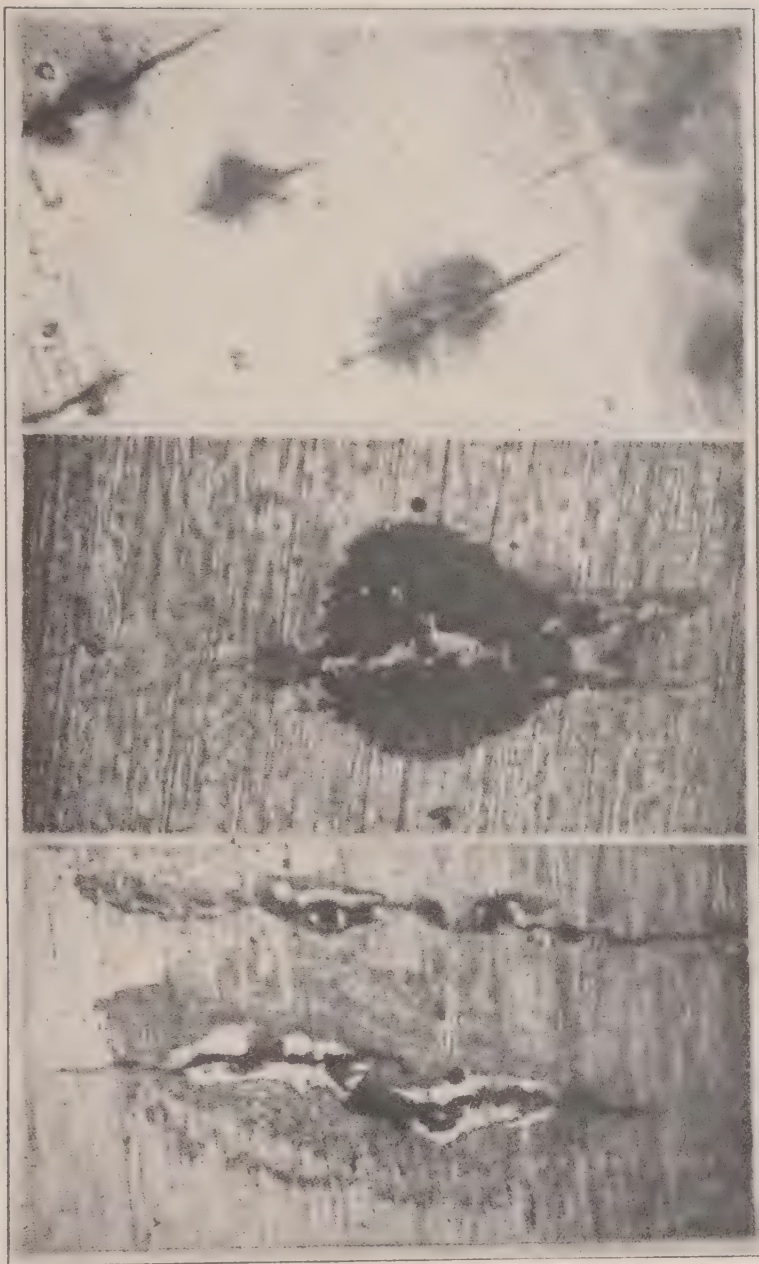
The cold drawn alloy tube on left is cracked completely through in a bad case of combined corrosion and internal stress.

The cartridge case below shows incipient cracking from same cause.

This may occur with little or no other visible sign of corrosion.

Photographs reproduced by permission from paper by Moore, Beckinsale and Mallinson, *J. Inst. Met.*, **25**, (1921) 37.





CORROSION FATIGUE

Typical cracking on steel surface by combined action of corrosion and alternating stress. $\times 100$.

Reproduced by permission from article by D. J. McAdam, *Trans. Am. Soc. Steel Treating*, 11, (1927) 374.

COMPOSITION AND HOMOGENEITY

If we consider this subject in the broadest sense, including all possible alloy combinations of metals it is possibly too complicated for practical conclusions at the present time. We can only make useful statements on some particular phases.

The two classes of alloys useful on account of their corrosion resistance, are those whose combining affinity is too low to react, and those which readily form preventive films, when in contact with corrosive materials. In both classes there is wide latitude for composition variation. A noble metal may often be alloyed with considerable quantities of a metal of high combining tendencies with little change in its corrosion resistance. In fact the first change may be toward better corrosion resistance as the less noble metal is added in small increments. Many cases of specific resistance to corrosion are known wherein an alloy is more resistant than any of its constituents. In the same way the film-protected type of corrosion resistance may exist with considerable variation in the film-forming constituent. As long as it is present in sufficient quantity to produce a continuous film under conditions of use variation is entirely permissible.

Homogeneity, however, is almost always a promoter of high corrosion resistance, and therefore highly corrosion-resistant alloys are largely solid solutions. The presence of more than one phase may set up galvanic cells in the noble type of alloys and may cause film discontinuity in those protected by films. Even a small percentage of a second phase may be quite destructive to protective films, but small amounts of a less noble phase in a noble alloy will have little or no effect in final corrosion resistance. In the latter case it seems necessary to have a quantity sufficient to give a continuous network to be seriously destructive. Easily corroded materials are of course very deleterious when present in grain boundaries since when they are present a small amount of actual corrosive reaction will destroy the soundness of a relatively large quantity of metal.

One method of being certain of homogeneity is making a metal so pure that there is no foreign material which can possibly separate from the parent mass. This procedure has in cases produced metals with corrosion resistance very much higher than would be expected from the properties of ordinary commercial forms. This is not universally the case, however.

It seems, then, that while homogeneity of composition is desirable and is in no case disadvantageous in a corrosive sense, it cannot be said that variation in composition will necessarily cause corrosion troubles. In many cases lack of homogeneity produces improvement in other properties of much greater importance than the slight effect on corrosion resistance. While heterogeneity may always be looked on with suspicion it is not *per se* indicative of corrosion failure.

STRAINS

Metal deformation has been connected with corrosion failure in numberless instances. But like many other phenomena connected with corrosion it is easy to attribute more failure to this one cause than is really justified. For instance, the very common presence of local corrosion at a point where two metals bear on each other mechanically can be attributed to strain, to galvanic contact or to electrolytic concentration cells depending on which of these magic corrodors is our favorite hobby. Certain it is that all three will exist in such a case and any one of them may cause serious effects. It is also certain that in the atmosphere such a mechanical bearing can hold corrosive dampness while exposed surfaces in the neighborhood are dry, but such an explanation is too simple to have the proper appeal.

There can be no question of the part which strain plays in corrosion cracking and corrosion fatigue (which see) and likewise strain probably causes some increase in corrosion whenever it exists. These effects on general corrosion however are likely to be less in magnitude than other variables which are usually present and which may be so connected in their origin with the existing strain as to be difficultly distinguished. Where a great tendency toward local corrosion exists local strains may be sufficient to allocate the corrosion. If two portions of metal otherwise entirely alike are in electrical connection in a homogeneous solution the probability is that the one which is more strained will corrode to a greater extent and the less strained material will act to a certain extent as a cathode. But many of the other factors discussed above are sufficiently strong to upset this effect if they happen to be so directed.

Metal is said to be "over strained" when it has been so deformed that ordinary heat treatment and proper work does not bring it back to its normal physical properties. In this condition certain corrosive effects are very much more destructive than on normal metal. In this condition a relatively mild corrosive will often attack a resistant metal locally and cause rapid failure. This condition always exists on raw sheared edges. Often a finish shaping operation such as an indenture in a sheet will cause overstraining which would not otherwise be discernible but which will cause local failure under mild corrosive action.

SURFACE

The initial state of a metal surface in corrosion will have considerable effect on the initial potential and corrosion rate and under some circumstances this initial effect will be so continued as to change the whole corrosive action. While these facts are rather widely recognized there is relatively little quantitative data on the effect of different types of surface.

While it might be expected that the rapidly corrodible parts of a surface would be removed and action then settle down to a rate depending on the unchanged interior this is not always the case. The initial corrosion, especially if it be somewhat localized, leaves its mark in either further surface irregularities or in corrosion products. These, in their turn, may have a large effect on the progress of corrosion and thus the initial effect is continued over extended periods. Effects are of course dependent on the particular metal and its environment and any general rules will have many exceptions.

On metals which would otherwise form a continuous protective film in a given corrosive, some initial surface irregularity will produce irregularity in this film so that it never reached its proper protecting value before failure occurs. A rapid initial corrosion rate may produce a mass of corrosion product abnormal in its composition and thus interfere with the normal production of a protective film. On metals which do not form protective films composition differences or other irregularities may cause the beginning of pits whose action may extend to some depth. Adhering scale, surface inclusions, laps or blisters are liable to set up galvanic or concentration cells which will accelerate or localize corrosion to an indeterminate extent.

While these surface effects are of considerable importance there is little reliable data on either general or specific conditions and the engineer must at present exercise judgment in estimating how extensive these surface effects are liable to be under the conditions in which he is interested.

METAL CORROSION PROPERTIES

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The conclusions given in the preceding pages have been taken from the publications of the following workers, and the writers' own experiences. The authors wish to express appreciation of their valuable data.

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Boulanger, C.
Brennert, Sven
Desch, C. H.
Evans, U. R.
Friend, J. N.
Guertler, W. M.
Haase, L. W.
Hedges, E. C.
Herzog, E.
Homer, C. E.

Hudson, J. C.
Langmuir, I.
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Rollaston, E. C.
Taylor, H. S.
Theil, A. and C. Kayser
Tronstad, L.
Vernon, W. H. J.
Waldron, L. J. and E. C. Groesbeck



INTERGRANULAR CORROSION

Right.—Shows corrosion in valve casting.

Left, Upper.—Edge of corroded area ($\times 100$) showing the corrosion following grain boundaries.

Left, Lower.—Uncorroded area ($\times 1000$) showing the grain boundary precipitation which invites attack as above.

PART II

Corrosion Behavior of Specific Metal and Alloy Groups



Introductory

Useful generalizations on corrosion behavior are difficult of expression. The reason lies, of course, in the extremely complex nature of corrosion, each corrosion rate representing only the final result of the interplay of a great many physico-chemical responses.

Until recent years, a corrosion rate was considered more or less an absolute value, as applying to a given metal in a given solution. Now the investigator appreciates that the conditions of exposure should be known in detail for the rate to be interpreted properly. Ideally, he wants to know whether or not he must consider impurities in the solution, the degree of aeration, the temperature, the motion, the surface condition of the metal before exposure, reproducibility, and a number of other factors; and he wants to know how closely controlled these conditions have been during test.

Most corrosion tests are made with insufficient control of conditions. This is an unfortunate fact, but it does not mean that the data are valueless. Very few data are entirely without value. Once it is recognized that the conditions of a test were not closely controlled, the data may be given a broader interpretation. If a rate of 37.5 mg. per sq. dm. per day is obtained in a simple immersion beaker test—not a closely controlled type of test—this may be interpreted to mean that a rate somewhere between 25 and 50 mg. per sq. dm. per day might be expected in quiet totally submerged exposure in solution of low degree of aeration. The test has not been entirely valueless even though not closely controlled as to conditions. It is worth knowing that the action is more intense than 1 mg. per sq. dm. per day and that it is not 100-200 mg. per sq. dm. per day. In other words the test has served as an orientation.

The mistake is often made of giving corrosion rate data too literal an interpretation. Where conditions have not been closely controlled and are not clearly expressed the rates should be considered approximations.

Generalizations have been freely attempted in the following pages. In some cases the qualifying remarks may not be as complete as desired, yet if these were to be complete in every case the book would be interminably long and repetitious. It is presumed that the reader will acquire sufficient understanding of corrosion factors to give proper interpretation to the rates

TABLE 3.—Corrosion Rates—A Cross Section.
(Expressed in mg. per sq. dm. per day)

Metal	Acid		Alkaline Sodium Hydroxide—5%	Neutral		Air Normal Outdoor Urban Exposure
	Non-oxidizing			Fresh Water	Salt Water	
	Sulfuric—5%	Acetic—5%				
Aluminum	15-200	1-10	25,000	0-1	1-100	0-1
Zinc	High	3000-4000	75-1000	3-50	3-50*	0-2
Tin	10-2000*	10-2000*	500-800	0-3		0-1
Lead	0-10	100-1000*	1000-50,000	<1-10	2-50	0-1
Iron	100-2000*	50-2000	5000-50,000	1-35*	1-35*	5-40
Silicon Iron	0-1	0-1	0-1			
Stainless	0-500†	0-2	0-10	0-1	0-1000†	0-1
Copper Group	10-300*	10-80*	1000-10,000	0-5	1-75*	0-1
Nickel Group	10-200*	10-60*	1000-10,000	0-1	0-6	1-2

Note: Italics indicate no usefulness.
* Aeration leads to the higher rates in the range.
† Aeration leads to passivity, scarcity of dissolved air to activity.

and to fill in "between the lines" when noting generalizations. This background can be acquired from a study of the pages of Part I.

In presenting corrosion data the authors felt it better to use each metal or metal group as the unit on which to build, rather than each corrodent. This system of presentation has the shortcoming, it is true, that the answer to the question "what metal is the best to use?" or "is copper better than lead for sulfuric acid?" may not be so readily apparent. On the other hand, error and misinterpretation are far less likely to enter if the reader, in seeking an answer to questions such as these, should first determine the two or three types of metals that would seem to have virtue with the corrodent he needs to handle—perhaps using Table 3 as an indication,—then to study the paragraphs and data for this corrodent in the appropriate chapters. There are far too many cases where comparative rates for various metals under a single set of conditions invite misinterpretation. It is seldom that rates in a single set of closely controlled conditions alone give the *best* indication of behavior in a projected commercial use. The exposure conditions in use are normally quite unlike those in a controlled test. Seldom is a single rate derived under the more or less ideal conditions of a laboratory test sufficiently informing in itself when considering use. The correct interpretation of the rate requires consideration of other rates derived from tests under somewhat altered conditions.

A specific example will be useful. It is desired to know whether copper or 18-8 stainless steel would be better as a construction material for a tank to hold a quiet acid solution. It is found in a quiet beaker test, the specimens being totally submerged, that the rate for copper is 10 mg. per sq. dm. per day and that for 18-8 less than 1 mg. per sq. dm. per day. Both rates are low and consistent with long life. Since a copper tank of the type desired is cheaper, such a tank is installed. Much to the dismay of those responsible, the tank suffers premature failure at the solution level, the rate of penetration being about 25 times more rapid than calculated from the results of the beaker test. Presumably the tank should have been made of 18-8, and therefore a new 18-8 tank is installed. *Mirabile dictu*, this tank fails at the bottom by isolated pitting, in even more rapid time than the copper.

The beaker test had indicated truly enough the behavior of the two metals in quiet, partially aerated submersion. The unexpectedly rapid corrosion of the copper was due to the fact that the acid at the solution level was much more highly aerated than that against the copper specimen, plus the fact that corrosion products built up on the metal at the solution level, and these led to accelerated concentration cell attack. The pitting of the 18-8 on the other hand developed through local insufficiency of aeration and consequent failure of the protective film to be maintained.

It is evident therefore, that a single set of comparative corrosion rates is apt to lead to misinterpretation. Were rates comparing metals freely given in this book, the authors feel, confusion would result in far more cases than under the method of treatment actually followed, namely, covering each metal or "family" of metals separately.

The cross-section of corrosion rates, given in Table 3, serves a double purpose. First, the reader may find it useful as a generalized comparison of behavior among the metals. Second, he may find it very helpful in acquainting himself with the significance of the unit of corrosion rate used in the chapters following—mg. per sq. dm. per day.

Several units are used in the literature in the expression of corrosion rates. In this book the unit "mg. per sq. dm. per day" has been chosen as being the most expressive. This unit, which comes readily and without much chance of error from service and laboratory measurements, gives an unusually convenient system for expression and memory. Decimal points are usually unnecessary. Zero mg. per sq. dm. per day is roughly the lower limit of measurement and represents "no practical corrosion." One to ten represents very slight attack. From ten to one hundred the corro-

TABLE 4.—Conversion of Corrosion Rates.

(Mg. per sq. dm. per day $\times \frac{.001437}{\text{density}}$ = inch per year)

Metal	Mg. per sq. dm. per day	Inch per year	Cm. per year
Magnesium group	100	.081	.206
Aluminum group	100	.053	.135
Zinc	100	.020	.050
Lead	100	.013	.032
Cadmium	100	.016	.041
Tin	100	.020	.050
Iron and steel	100	.018	.047
Cast iron	100	.020	.051
Silicon iron	100	.020	.052
Stainless iron (14 Cr)	100	.019	.048
Stainless steel (18 Cr 8 Ni)	100	.018	.046
60 Ni 15 Cr 25 Fe	100	.018	.046
60 Ni 20 Mo 20 Fe	100	.016	.041
80 Ni 14 Cr 6 Fe	100	.017	.043
Nickel	100	.016	.041
Monel metal	100	.016	.041
Copper	100	.016	.041
Brass (65 Cu 35 Zn)	100	.017	.044
Bronze (3 Si 1 Mn)	100	.017	.043

sion must be taken into consideration and rates near one hundred are liable to be serious. From 100 to 500 conditions are serious and rates above 500 usually represent corrosion failure. While it is obvious that such generalizations must be limited by the "form of corrosion"—Chapter II—the convenience of expression and calculation as indicated seem to justify the use of this unit and it goes without saying that a single unit is better than a mixture.

Rates so expressed may be converted into "inch per year" and "centimeter per year" by the factors given in Table 4.

A TABLE OF STRENGTH AND DUCTILITY OF METALS.

Metal and Condition		Tensile Strength lbs. per sq. in.	Ductility
Magnesium	Wrought, Soft ¹	25,000	Low
Magnesium alloy (4 Al 0.3 Mn)	Wrought, Soft ¹	35,000	Fair
Aluminum	Wrought, Soft ¹	12,000	Good
Aluminum (1.5 Mn)	Wrought, Soft ¹	16,000	Good
Duralumin	Wrought, Soft ^{1, 2}	30,000	Good
Zinc	Wrought, Soft	24,000	Good
Lead	Wrought, Soft	1,750	Good
Lead alloy (4 Sb)	Wrought, Soft	4,000	Good
Tin	Wrought, Soft	5-6,000	Good
Wrought iron	Wrought, Soft ¹	45,000	Good
Mild steel	Wrought, Soft ^{1, 2}	70,000	Good
High carbon and alloy steels	Wrought, Soft ^{1, 2}	90,000	Good
Cast iron	Cast	30,000	Low
Alloy cast iron (14 Ni 6 Cu 3 Cr)	Cast	30,000	Low
Silicon iron (14 Si)	Cast	10,000	Very low
Stainless iron (14 Cr)	Wrought, Soft ¹	80,000	Good
Stainless steel (18 Cr 8 Ni)	Wrought, Soft ¹	85,000	Good
Nickel-iron alloy (36 Ni)	Wrought, Soft ¹	65,000	Good
Heat-resistant alloy (60 Ni 15 Cr 25 Fe)	Wrought, Soft ¹	90,000	Good
Nickel	Wrought, Soft ¹	60,000	Good
Monel metal	Wrought, Soft ¹	65,000	Good
Copper	Wrought, Soft ¹	30,000	Good
Brass (65 Cu 35 Zn)	Wrought, Soft ¹	45,000	Good
Bronze (4 Sn)	Wrought, Soft ¹	50,000	Good
Bronze (3 Si 1 Mn)	Wrought, Soft ¹	50,000	Good
Bronze (5 Sn 5 Zn 5 Pb)	Cast	26,000	Fair
Nickel silver (17 Zn 18 Ni)	Wrought, Soft ¹	50,000	Good

¹ Can be strengthened with cold-work.

² Can be strengthened by heat-treatment.

A TABLE OF PHYSICAL CONSTANTS OF METALS.*

Metal	Specific gravity	Melting point ° F.	Coefficient of expans. per ° C.	Heat conductivity cal. per cm. per sec.	Electrical resistivity Micro.-cm. cube	Modulus of elasticity
Magnesium	1.74	1204	.000026	0.38	4.5	6,500,000
Aluminum	2.7	1215	.000024	0.52	2.6	10,000,000
Zinc	7.2	786	.000039	0.26	5.8	15,000,000
Cadmium	8.6	608	.000031		6.2	
Tin	7.3	450	.000021	0.15	11.5	5,700,000
Lead	11.3	621	.000029	.082	22	2,560,000
Wrought iron	7.7	2800	.000013	0.16	10	25,000,000
Mild steel	7.9	2550	.000012	0.13	18	30,000,000
Cast iron	7.2	2100	.000010	0.10	113	8-12,000,000
Silicon-iron alloy (14 Si)	6.9	2300	.000028		63	
Stainless iron (14 Cr)	7.7	2714	.000011	.09	64	30,000,000
Stainless steel (18 Cr 8 Ni)	7.9	2640	.000017	.07	78	28,600,000
Nickel-iron alloy (36 Ni)	8.3	2600	.000003		80	21,400,000
Heat-resistant alloy (60 Ni 15 Cr 25 Fe)	8.2	2462	.000014		112	
Nickel	8.85	2624	.000013	0.14	10.9	30,000,000
Monel metal	8.80	2460	.000014	.06	42.5	26,000,000
Copper	8.9	1981	.000016	0.89	17	16,000,000
Brass (65 Cu 35 Zn)	8.5	1680	.000020	0.29	6.68	15,000,000
Bronze (4 Sn)	8.8	1740	.000017		12.4	16,000,000
Bronze (3 Si 1 Mn)	8.45	1920	.000017	.078	27.7	15,000,000
Nickel silver (17 Zn 18 Ni)	8.75	2030	.000018	.079	30.7	17,000,000
Silver	10.5	1760	.000019		1.6	9,000,000
Gold	19.2	1945	.000014		2.4	11,100,000
Platinum	21.5	3191	.000008	0.16	10	23,000,000

* Taken from many sources; sufficiently accurate for comparison.

Chapter V

Magnesium and Its Alloys

The lightness of magnesium is a remarkable property. Its specific gravity is 1.74 as compared with 2.7 for aluminum and 7.8 for iron. Lightness is practically always a virtue, in the use of metals. Fortunately this property is made available, in magnesium, through the fact that magnesium alloys have a good degree of strength—entering the range covered by the aluminum group of metals—and a very serviceable corrosion resistance in atmospheric exposure.

The present-day commercial application of magnesium alloys includes equipment and parts in the fields of aeronautics, automotive transportation, portable tools, general machinery, office equipment. In uses of this nature the alloys are often painted, both for the purpose of improving atmospheric resistance and to give desirable artistic finishes.

The alloys most widely used in this country are the group carrying 4 to 10% aluminum and 0.2 to 0.4% manganese, with or without 0.5 to 3% zinc. The higher range of aluminum, or aluminum plus zinc, is generally recommended for castings and the lower for wrought metal. These alloys are far stronger than pure magnesium. Binary alloys carrying 1.25 to 2.0% manganese are used less widely, because of less strength, but have better resistance to sea water.

It has been found* that the corrosion resistance of the alloys is influenced to a rather marked extent by the alloying elements. Manganese, as already stated, is added to improve resistance to sea water. The heavy metals, such as copper and nickel, are definitely damaging when present even to the extent of 0.1%.

In corrosion resistance the magnesium alloys up to the present time are definitely less versatile than the aluminum alloys. On the other hand they just as definitely have their virtue. Thus in atmospheric exposure magnesium develops an oxide film that is highly protective. In rural and industrial atmospheres magnesium is usefully resistant, although the resistance tends to break down where the atmospheres carry salt and particularly salt

* J. A. Gann, private comment.

spray. In waters, generally speaking, the magnesium metals are not useful in their present stage of development. In acids, with the exception of hydrofluoric acid solutions, and possibly one or two others, magnesium has no important degree of resistance. In hydrofluoric acid, curiously enough, the film that forms on the alloy is very highly protective. Hydrochloric acid on the other hand finds the resistance of magnesium very low. Again, in caustic solutions magnesium develops a highly protective film, its resistance being far greater than that of the aluminum metals.

It is stated by Gann⁴ that there is no loss in strength or ductility of magnesium alloys, from exposure, that can be attributed to intercrystalline corrosion.

THE PROTECTIVE OXIDE

Metallic magnesium has a strong affinity for oxygen. In the degree of power of its tendency to combine with oxygen, it falls between silicon and aluminum. Like that on aluminum and unlike that on silicon the oxide is protective, and the progress of oxidation of freshly surfaced metal is rapidly stopped. The behavior of magnesium in any medium consequently depends on what happens to the oxide—whether the oxide is penetrated, is dissolved, is damaged, or is prevented from forming.

The behavior of the film in salt solutions has been studied by Boyer.² He found that pure magnesium immersed in sodium chloride evolved hydrogen rapidly at first, visible evolution of hydrogen ceasing only after about 26 hours. It may be considered that the slowing down of the evolution was due to the slowing down of the rate of supply of reactants through the film to the surface of the metal itself. Metal in this corroded condition was found capable of acting cathodically to metal previously unexposed, and anodically to platinum. When magnesium was coupled with platinum, hydrogen was immediately evolved with vigor at both electrodes. Boyer concluded that the overvoltage of magnesium together with ennobling from the corrosion product film was sufficient to put a stop to hydrogen evolution. Undoubtedly the nature of the solution at the unattacked metal changes as the oxide film develops; Boyer's experiments indicate that the nature of the film is such that it is seemingly more capable of supporting the anodic than the cathodic reaction. The effect of the oxide is to slow down diffusion rates and so aid in the change in nature of the solution.

TWO-METAL GALVANIC BEHAVIOR

Magnesium is the least noble of the useful metals listed in the usual electrochemical series. As a consequence, in galvanic couple magnesium tends to suffer, whether the metal coupled with it be aluminum or any one of the more noble metals. It is for this reason that magnesium metals may not

with safety be used coupled even with aluminum in the presence of moisture. The problem of galvanic attack often can be overcome through properly insulating magnesium from the more noble metal. Paints, such as reinforced red lead and bitumastic materials are satisfactory insulations.*

Coupling with a more noble metal, such as aluminum, leads to a change in the protective film on magnesium of such a sort that the cathodic reaction is accelerated on the magnesium as well as taking place on the more cathodic metal, the combined attack becoming great. At least, this phenomenon has been observed in exposure to salt water. In three-hour tests⁶ in 3% sodium chloride hydrogen gas evolved as shown in Table 5 from the coupled metals.

TABLE 5.—*Magnesium Couples in Sodium Chloride.*

Other metal	Cu. Cm. Hydrogen Evolved	
	At other metal	At Magnesium
Platinum	142	110
Aluminum	126	80
Iron	58	70
Nickel	45	55
Copper	28	43
Lead	22	34
Manganese	13	22
Zinc	6	15
Magnesium alone		13

The total hydrogen evolved from the aluminum:magnesium couple was sixteen times that from uncoupled magnesium. The damaging effect of zinc seems to be slight, a fact that may reasonably lead to the successful coupling, commercially, of galvanized iron and magnesium in atmospheric exposure.

Coupling with mercury leads to no anodic attack of magnesium,^{2,6} insofar as appreciable hydrogen evolution is an indication. The reason for this lies in the fact that the high overvoltage of mercury prevents the flow of current.

PITTING

The magnesium alloys normally pit in salt solutions. Boyer² has observed that the pitting is not related to a heterogeneous structure. He has noticed that in the progress of pitting hydrogen is evolved from the pit itself, and has suggested that the magnesium chloride formed in a deepening pit sets up an acid condition that is favorable to continued penetration.

* J. A. Gann, private comment.

ATMOSPHERE

The behavior of the magnesium alloys in atmospheric exposure is, naturally enough, the most important feature of their corrosion resistance. There is not available as yet a body of quantitative data to outline fully what may be expected of them. Bengough and Whitby¹ have made tests of three-years duration, in which various magnesium alloys were exposed outdoors, unprotected from the rain, at Teddington, in the environs of London. They found the particularly interesting fact that corrosion, though very slight, remained progressive over the three-year period.

A slow increase in weight was noticed, even in dry periods. The increase was followed, in rainy periods, by a decrease. The actual weight-loss corrosion rates over the period ran less than 1 mg. per sq. dm. per day, which is on the order of rates for metals like zinc under similar circumstances. This rate corresponds to .0008 inch per year. The magnesium alloys in the present tests were finely pitted.

According also to Bengough and Whitby,¹ dry air at laboratory temperature had little or no action on magnesium, the rate of attack increasing with humidity to the point where, at 90% of saturation, the attack was rapid. The corrosion product layer that first formed; under the more humid conditions, was granular and not at once protective. They found the corrosion product, after 400 days in indoor exposure, carried carbonate and sulfate as well as hydroxide.

Magnesium alloys normally turn a dark gray in atmospheric exposure.

In the use of the magnesium alloys it is well not to allow rain or atmospheric moisture to be trapped at any point, since this leads to greatly exaggerated corrosion.

The acid formed in moist industrial atmospheres appears to be damaging to magnesium, as mentioned by Horn.⁵ Certainly the salt moisture of sea air is damaging. Sutton and LeBrocq⁷ tested magnesium alloy specimens, previously treated in a bath of hot potassium dichromate, potash alum, and caustic soda, followed by a lanoline coat, and these remained in good condition over a fifteen-month period on the instrument board of a seaplane. Other specimens, fastened on the tail section, were badly pitted in less than two months, particularly where in contact with fabric.

PROTECTION

Methods of protecting magnesium alloys have been rather widely investigated. The most successful method seems to be a chemical treatment followed by coatings of paints. Metallic coatings do not seem to have virtue. From the standpoint of two-metal galvanic relations, zinc—and possibly cadmium—alone might have virtue, if they could be satisfactorily deposited

though even this is somewhat doubtful. There are technical obstacles, seemingly impossible to avoid, in coating magnesium electrolytically. Nor has anodic oxidation been found to be of any use with magnesium alloys.

Chemical treatment is for the purpose of preparing the surface to take the subsequent layer of paint or other protective coat. The treatment used largely in this country and abroad is known as the "chrome pickle," and consists of a $\frac{1}{2}$ - to 2-minute dip in a solution of sodium bichromate ($1\frac{1}{2}$ lbs.), concentrated nitric ($1\frac{1}{2}$ pts., of spec. grav. 1.42) and water (to make 1 gal.).*

Another method advocated in England, is immersion in a hot aqueous solution of potassium dichromate, potash alum and caustic soda.^{5, 7}

The application of paints, following chemical treatment, is customary practice. Bengough and Whitby¹ state that chemical treatment followed by paint or lanoline has given twenty-fold or more increase in resistance, (presumably in accelerated tests). Actually all types of paints, varnishes, lacquers, and enamels are serviceable, although the performance varies tremendously within each group. The selection of a protective coating should follow careful preliminary tests.

SALT WATER

The protection of magnesium alloys by these means provides for improved resistance against the atmosphere, even when of the more corrosive types. In fact the service performance of the alloys when properly painted is strictly commercial. Against salt spray or in submerged salt water the protection is considerable yet not sufficient to warrant continuous exposure. Coatings or paints are always penetrable, and salt moisture is rapidly damaging to magnesium. Sutton and LeBrocq⁷ have reported a corrosion rate, in 5-weeks exposure to sea water spray, of 20 mg. per sq. dm. per day (.016 in. per year) or greater for an uncoated alloy carrying 1.85% manganese, and 3 times this rate for pure magnesium. This of course is a very damaging attack. Boyer² has given rates ranging from 300 to 18,000 mg. per sq. dm. per day for various magnesium alloys in intermittent exposure for 48 hours in a 2% sodium chloride solution. Boyer's results have shown that, under this exposure condition, increasing the aluminum content of the alloys from 2 to 8% has led to much greater attack. And he brought out particularly the beneficial effect of manganese. He tested specimens of a 4% aluminum magnesium alloy both with and without 0.3% manganese and obtained the results in Table 6.

TABLE 6.—*Magnesium-Aluminum Alloys vs. Salt Water.*

	Mg. per sq. dm. per day
Without manganese	6,100 - 12,000
With manganese	340 - 560

* J. A. Gann, private comment.

The same base alloy with varying contents of manganese exposed 5 days in 2% sodium chloride gave the results in Table 7.

TABLE 7.—*Magnesium-Aluminum Alloys vs. Salt Water.*

Percent Manganese	Mg. per sq. dm. per day
.10	8,600
.15	8,500
.19	5,100
.23	4,000
.28	1,400
.32	990
.38	760
.40	850

Gann ⁴ has stated that 0.3 to 0.5% manganese is the equilibrium concentration in alloys carrying 4 to 8% aluminum. According to Boyer,² the effect manganese has is to raise the hydrogen overvoltage of the alloy. This of course suppresses corrosion of the hydrogen evolution type.

FRESH WATER

Fresh waters are far less corrosive than sea water to the alloys, although there hardly is enough data to indicate just what behavior to expect. A four-months test on commercial alloys of the magnesium-aluminum-manganese type in distilled water has given a rate of about 1 mg. per sq. dm. per day, and a test in tap water carrying 100 parts per million sodium chloride gave a rate of about 3 mg. per sq. dm. per day.*

ACIDS

Acids, as already stated, normally attack magnesium. Action may be so strong as to be described as violent, in hydrochloric and nitric. Yet the resistance is so good against hydrofluoric acid that magnesium is used commercially for containers handling this. It seems that the attack is appreciable in the more dilute concentrations—less than 1%—yet practically negligible in solutions with more than 5%.* Solutions of 10% to perhaps 40% have been found to lead to corrosion of immersed magnesium alloys immediately above the level of the solution. No corrosion rates for hydrofluoric acid are available, unfortunately.

Magnesium is resistant to acid phosphates, chromates, bichromates, and dilute solutions of chromic acid, according to Gann.⁴

* J. A. Gann, private comment.

MAGNESIUM AND ITS ALLOYS

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Chapter VI

Aluminum and Its Alloys*

Resistance to corrosion, light weight, and good electrical and thermal conductivity are the characteristics accounting for the greater part of the uses of aluminum. The relatively low strength, and softness of the pure metal, undesirable qualities for many engineering purposes, are desirable where ease of forming is wanted. The large scale development of aluminum alloys has supplied the requirements of strength with light weight.

Commercially pure aluminum** carries less than 1% impurity; this grade is used in applications where good corrosion resistance is required and high strength is not necessary. A manganese content of 1½% improves the strength with no loss in general in corrosion resistance; to this, silicon is sometimes added for further strengthening. Of the light alloys characterized by high strength, duralumin is the most important, carrying 4% copper with 0.5% manganese and 0.5% magnesium. A second type of alloy whose strength is developed by heat treatment carries 4.4% copper, 0.8% silicon and 0.75% manganese. Still a third carries no copper, 1.0% silicon and 0.6% magnesium. Other strong aluminum alloys, wrought and cast, carry various combinations of copper, silicon, zinc, and magnesium. Duralumin carrying, for corrosion purposes, surface layers of pure aluminum is a common product in this country; it is known as Alclad.

From the standpoint of resistance, aside from commercially pure aluminum, the manganese alloy for wrought and the 5% or the 13% silicon alloy for castings seem to be the best.

Inherently one of the less noble metals, aluminum plays the role of a highly corrosion resistant metal by reason of the presence on its surface of a protective, tightly adherent, invisible and almost impervious coating of aluminum oxide. Aluminum oxide occupies a greater volume than aluminum,³² which would seem to be an important factor in its protective value. The oxygen or oxidizing substances in most solutions, and in the atmosphere, is sufficient to develop this protective film. Corrosion progresses by diffusion of oxygen or aqueous solutions through this film or by the dissolving away of the film. In strong alkaline and in strong acid solutions the oxide is soluble and the attack of aluminum pronounced. Some

* An excellent book on the subject is that of Edwards, Frary and Jeffries.³¹

** Aluminum of 99.99% purity has been produced.³¹

acids, notably concentrated nitric and all concentrations of acetic are very successfully handled with aluminum, since against these the oxide is stable and highly protective. In the neutral range of solution—waters, atmospheres, salts, etc.—resistance is generally good.

The oxide film on aluminum has been studied by a number of workers.^{11, 34, 72, 89, 96, 99, 100, 104} The thickness of film developing in air on freshly surfaced aluminum was found to be on the order of .000001 cm.¹⁰⁰

The potentials developed by aluminum in aqueous solutions, and variations in potentials with time, pre-treatment of the metal, and exposure conditions have been studied by various workers.^{6, 17, 18, 30, 35, 54} Callendar^{17, 18} measured the boundary resistance of specimens that had been resurfaced and exposed to air for various periods, the boundary resistance characteristic of different surfacing treatment and oxidizing treatment at elevated temperatures, and the change in boundary resistance with time. These resistances he attributed to oxide films and possibly gas films. Potential differences were obtained between freshly surfaced aluminum and aluminum previously exposed to the air. Kahlenberg and French⁵⁴ found an alteration in potential depending on whether oxygen, hydrogen, or nitrogen was passed into the solution, and believed the characteristic drop in potential of aluminum on immersion in solution carrying oxygen to be due to absorbed gas rather than to development of oxide.

TEST METHOD CONSIDERATIONS

The corrosion testing of aluminum has become rather complicated due to the various modes of attack it may suffer. Weight loss rates are satisfactory as an indication only so long as the corrosion is reasonably even in distribution, so long as there is no intercrystalline action, and so long as the oxide film as a factor in the weight change is not overlooked. Aluminum and its alloys often become pitted, and in this circumstance weight loss rates tell but a part of the story. Another fact limiting the import of the weight loss rate for aluminum is that in many cases the rate slows down with time. This decreasing rate is characteristic of aluminum in all types of exposure where the metal is useful and often in exposure where the action may be too great for it to be useful. A number of cases will be given later on.

Another method of expressing attack is in terms of rate of hydrogen evolution. This method is an expression of average attack and is used to compare behavior of different specimens,—the effect of impurities, alloying, heat-treatment,—rather than to give straightforward information on life-to-failure.

Duralumin that has been given improper heat treatment is subject to intercrystalline deterioration. Tensile tests before and after exposure have

been found the best means of measuring the damage from this source. In Table 8 is given a comparison of different criteria of attack of a single duralumin composition that has been aged at different temperatures.⁶⁸ The specimens were exposed three months in sea water and air just above half-tide level. The alloy carried 4.4% copper, 0.6% manganese, 0.5% magnesium, 0.8% silicon, and was quenched from a temperature of 932° F. and subsequently aged for 20 hours at room temperature, 212° F. and 284° F. respectively. The specimens were .078 inch in thickness.

TABLE 8.—*Duralumin vs. Sea Water and Air.*

	Aged at Room Temp.	Aged at 212° F.	Aged at 284° F.
Weight change, g. per sq. m.....	—6.5	—6.5	+16
Drop in tensile strength, %	6	6	57
Drop in elongation, %	47	39	95
Pitting	Yes	Yes	Yes
Intercrystalline attack	No	Yes	Yes

An even more sensitive test of damage than change in tensile properties is change in fatigue limit. Moore⁷⁰ has stated that fatigue strength drops 10 to 20 times as rapidly as tensile strength. Fatigue testing, however, is extremely inconvenient as a method of studying corrosion.

Different corrosive solutions and exposure conditions are used in testing the light metals—salt spray, simple immersion, intermittent immersion, artificial sea water, mixtures of salt and peroxide. Peroxide-salt solutions are strongly corrosive and can scarcely be expected to furnish same sequences of behavior among the alloys and the various heat-treatments as tests under conditions that are less corrosive, such as sea water and the atmosphere. Salt spray tests are particularly useful in searching for intercrystalline attack. Rawdon^{78, 79} has reported an encouragingly close parallelism between the results of laboratory salt water wet-and-dry tests and those of atmospheric exposure. He also has found⁷⁵ the spray test and continuous immersion test less drastic than the repeated immersion test.

INFLUENCE OF ALLOYING ELEMENTS

It is often considered that the purer grades of metal are the more resistant, a belief based on the theory that corrosion intensity is dependent largely on the number of galvanic couples. There is a great deal of data to show that this factor very often is unimportant. The reason for this may be understood when the light metals are visualized as carrying the protective oxide film, and the progress of corrosion as being determined by the behavior of the oxide, rather than the metal itself, in the corrosive agent. Under exposure conditions where the rate of attack is slow—as in ordinary atmosphere—the oxide is highly protective of course. Attack over as long

a period as 23 years in city air has been found¹⁰³ to be extremely slight, whether of pure aluminum or alloys with various more noble elements. One case where alloying becomes deleterious is as slow a corrodent as atmosphere is that of improperly treated duralumin. With this there seems to be sufficient penetration of active agent through the oxide to cause an intergranular penetration. But it is important to note that the alloy must be made susceptible to attack in the first place, by defective pre-treatment. The oxide on properly treated duralumin may be equally penetrable, but the damage does not take place, since the alloy is not receptive. Furthermore, it is not to be presumed that disintegration of duralumin necessarily is related to galvanic couples within the metal. It is sufficient to consider that the intergranular substance—of whatever its nature—alone is involved.

On the other hand, solutions that are rapidly damaging to the oxide film, either by dissolving it as in the case of caustic solutions or hydrochloric acid, or by penetrating it as in the case of chloride salt solutions, bring about a different situation. The solution comes more or less freely in contact with the metal itself rather than the oxide and if the metal is heterogeneous in structure corrosion intensity and distribution will be in part related to the minute galvanic couples. Here again, however, it is well to recognize that the purest aluminum conceivably would corrode rapidly—in general as rapidly as an impure aluminum—in any substance that dissolved or damaged or prevented formation of the oxide film.

The problem of the effect of alloying elements in aluminum has another feature that is important—with some alloying elements the protective film under a corrosion condition may become more fully developed than with others. The ordinary atmosphere does not seem to be such a corrosion condition, yet chloride salt solutions do. It might be considered that some alloying elements “dilute” the film-forming capacity of aluminum. This seems to be characteristic of copper, whereas silicon and manganese do not seem to have a damaging effect. Furthermore copper is far more damaging when it exists other than as a solid solution in the aluminum. It is conceivable enough that a protective oxide is developed with greater difficulty on Cu Al_2 than on the aluminum solid solution.

How then, practically, may the aluminum metals be expected to differ among themselves in corrosion resistance? Briefly, in the least corrosive mediums—such as rural and average urban atmosphere—the differences are slight, if recognizable at all, aside from changes in superficial appearance. In the more corrosive conditions of practical use—sea water, for instance—differences in behavior vary widely, the multiphase alloys, particularly when carrying copper or zinc, being poorer and the silicon or manganese alloys and pure aluminum being better. For handling acids ordinary aluminum and the manganese alloys alone are really suitable.

A great many investigations have been made on the effect of alloying elements and impurities on the corrosion of aluminum.^{2, 7, 19, 20, 25, 28, 31, 43, 44, 56, 67, 73, 78, 84, 92, 93} It would seem hardly worthwhile or useful to attempt a correlation of the data for this chapter, since it seems to the present authors that most of the data is rather remote from the question of where and where not the light metals can be used and what is the behavior to be expected. An exception is the data on intercrystalline corrosion of duralumin, to which attention will now be directed.

INTERCRYSTALLINE CORROSION

The danger of intercrystalline attack of duralumin,^{13, 14, 25, 50, 56, 68, 74-80, 94, 103} thanks to the work of Rawdon⁷⁴⁻⁸⁰ and others in recognizing the causes and to Dix²⁵ and others in developing preventive methods, is, at the present time, largely overcome. Rawdon⁷⁴ has said "it is now no longer a question whether or not the intercrystalline attack can be prevented, but merely which one of several effective methods should be chosen in a particular case." He also has stated "a great deal of the duralumin sheet examined after long service under rather corrosive conditions has not been found to be harmed, that is, in an intercrystalline manner, by time, exposure or use."

Dix²⁶ in two-year and five-year atmospheric tests, and in tests lasting two and one-half years in sea salt solution reported some damage from pitting. Presumably no intercrystalline attack took place. The damage was of a self-stopping nature, that occurring in 2 years or $2\frac{1}{2}$ years being no greater, materially, than that in 1 year, and that in 5 years no greater than that in 2 years. Others have noted the same thing.^{81, 98}

An indication of the good behavior of properly treated duralumin in a more corrosive environment than the atmosphere is given by salt spray test results.¹⁴ The tests ran up to seven months. Both ordinary duralumin and a modification with higher silicon and free of magnesium were quenched from 932° F.; the duralumin was aged at room temperature, the modification aged at a higher temperature. The treatment in each case was good normal procedure. Specimens were tested in three conditions: (1) after being plastically stressed, (2) stressed elastically during test, (3) a combination of the two. No intercrystalline failure of the duralumin was found on microscopic examination to have occurred. The modification failed under elastic stress, even when of slight amount (5500 lbs. per sq. in.). Plastic stress of the modified alloy did not in the absence of elastic stress cause failure, yet it hastened failure of specimens elastically stressed at the same time. Rawdon⁷⁸ also found that the cold working of properly treated duralumin had no appreciable influence towards making the alloy susceptible to intercrystalline embrittlement.

Specimens of a duralumin alloy carrying 0.8% silicon were exposed three months at half-tide level on the North Sea.⁶⁸ The metal was prepared by quenching from 930° F. in cold water. Specimens aged at room temperature, though pitted, suffered no intercrystalline attack. Specimens aged at elevated temperature suffered intercrystalline attack.

These results of exposure in the atmosphere and in salt solutions illustrate the normal good behavior to be expected of properly treated duralumin.

The mechanism of intercrystalline embrittlement of duralumin is not as yet clear, the agency that makes an alloy susceptible being, it is believed, sub-microscopic. The copper in duralumin passes into solid solution at over 930° F. Quenching from this temperature range followed by room temperature ageing supplies in ordinary duralumin both desirable mechanical properties and resistance to intercrystalline embrittlement on subsequent exposure. Delayed cooling to room temperature or subsequent ageing at an elevated temperature destroys the resistance to embrittlement. It seems to be generally assumed that the active substance is Cu Al_2 , and that precipitation of this substance must be suppressed within some limit for the alloy to be resistant. The role that other elements—silicon, manganese, iron, magnesium—may play in the problem is still largely undetermined.

The cast alloys do not usually seem to be susceptible to intercrystalline embrittlement, although cases have been observed⁹⁴; alloys with 4% copper and 2% silicon, and those with 4 to 5% copper and 1% silicon are stated to be inferior from the intercrystalline standpoint. Pure aluminum and manganese aluminum,²⁵ and the copper-free alloy with 1% silicon and 0.6% magnesium are immune.

LOCALIZED ACTION

Pitting is a common occurrence with aluminum⁴³ and particularly with its alloys. Although the cause may be attributed to several factors—impurities, minute cavities, differential oxygen cells, adherent dust and dirt particles, air bubbles, emery particles—these all act through local breakdown of the oxide skin or local failure of the skin to develop in full protective degree. Callendar¹⁸ has demonstrated that a potential difference may exist between aluminum surfaces on which the oxide skin is developed in different thickness, and that the film forms slowly in air and alters slowly on immersion. These features lead to the reasoning that local obstruction to film development in air or on immersion may lead to the setting up of such potential differences and consequent flow of current. An even distribution of the film, Callendar suggests, may be prevented by settling of dust, grease, moisture, and by irregularities in the surface itself, the anodic areas being those of relative inaccessibility. Evans³³ has shown that aluminum, like other metals, is sensitive to differential aeration cell action;

cavities and foreign particles and even air bubbles^{33, 37, 89} are sufficient at times to lead to such cells. Points at which corrosion is taking place may remain of microscopic size,³⁸ and their location may be determined by bluish marks, cut edges, groove lines on abraded surfaces.³⁷ Aeration conditions favor more rapid attack at the water-line zone.

Pitting is most frequently associated with chloride salt exposure conditions, such as sea water and marine atmospheres; yet pitting of aluminum has been observed in tap water after a day or two exposure.⁸⁹ In atmospheric exposure, pits were in evidence on 99.9% aluminum after six months (marine and inland) and on properly heat-treated duralumin after 1½ months (marine).⁷⁸ Little information exists on the change in pitting rate with time; in aerated tap water the rate in one test series slowed down with time over periods of 60 to 100 days, the pitting intensity being more marked with duralumin than with the 1¼% manganese alloy.^{62, 64} Good evidence exists of the slowing down of pitting rates in atmospheric exposure.^{28, 78} The strong alloys are stated to be more sensitive to pitting than the purer grades.^{25, 31, 78}

Pitting seems to be associated often with cavities and fissures in aluminum. Guertler⁴³ and Rohrig⁸³ have called attention to the possibility of cavities being formed on aluminum surfaces by the fracturing of the silicon, iron-aluminum, and non-metallic constituents. Guertler has observed a dependence of corrosion on large silicon crystals and has suggested heat-treatment of commercial aluminum to put the silicon into the form of small grains (annealing over 750° F. with rapid cooling). It may be that cavities of this source become seats of the pitting attack so often observed in water-line areas.^{10, 23, 43} Seligman and Williams⁸⁹ were able to produce pitting in hard industrial waters at small artificial impressions closed over by hammering.

EFFECT OF STRESS

A sensitive criterion of corrosion damage is the drop in fatigue limit, since both corrosion and fatigue are essentially surface effects. With fatigue strength as a gage, damage to metal in both the unstressed and the stressed conditions has been determined.^{59-65, 70, 80} Important results are given here:

1. Significant damage to commercial aluminum, 1¼% manganese aluminum, duralumin, and other light alloys tested, results from an exposure in an unstressed condition to water of either low chloride content (tap water) or high (sea water), in a relatively short time. The drop in fatigue limit from tap water exposure for commercial aluminum is shown in Table 9 and for duralumin and manganese-aluminum in Figure 9.

FIGURE 9. Duralumin and Manganese-Aluminum Alloy vs. Fresh Water.

TABLE 9.—*Aluminum vs. Tapwater.*

Hours	Resultant Fatigue Limit lbs. per sq. in.
0	10,250
1	9,250
8	8,300
24	7,700

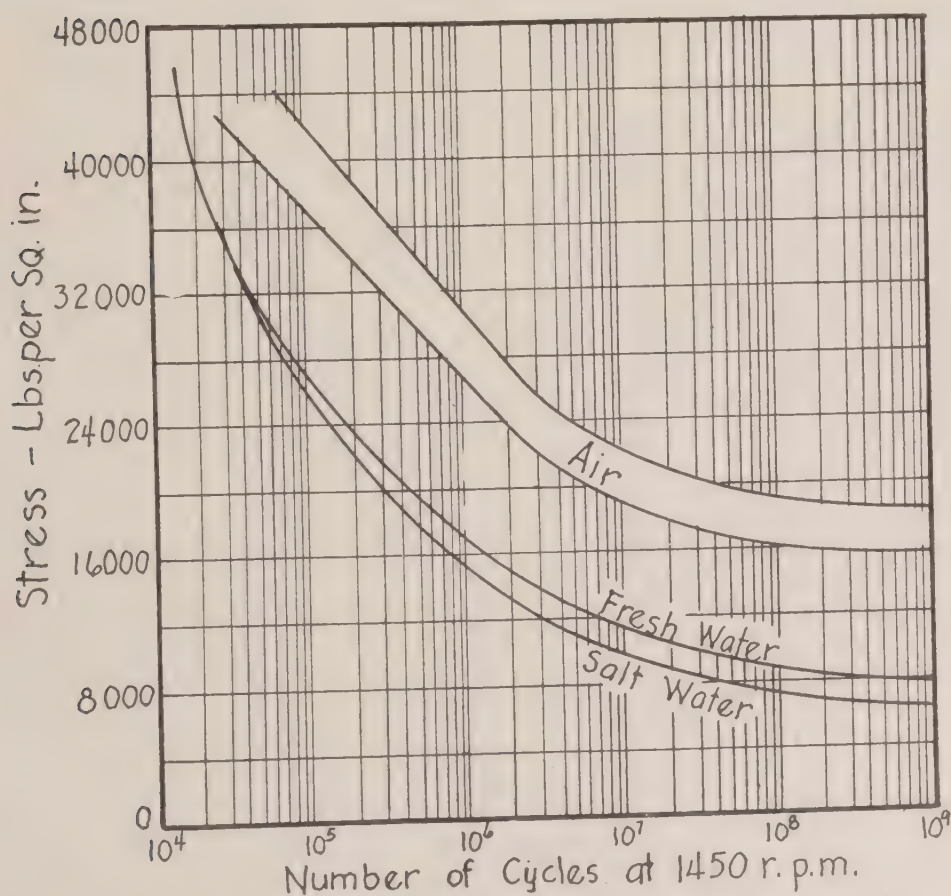
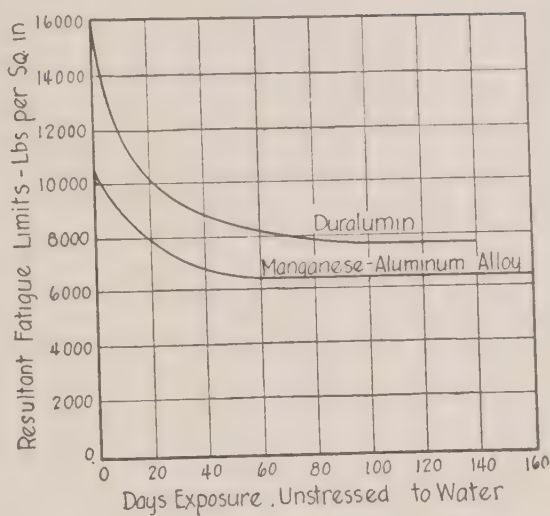


FIGURE 10. Duralumin (heat-treated) Tested in Fatigue in (1) Air, (2) Fresh Water Stream, (3) Salt Water Stream.

The rate of damage under these test conditions decreased steadily with time, becoming negligible after 100 days, more or less.

2. Exposure, simultaneously, to fatigue stresses and corrosion results in a lowering of the fatigue (stress-cycle) curve. Curves are given in Figure 10.
3. Stress accelerates the rate of corrosion damage, the effect being more pronounced with higher stress and with higher cycle frequencies. Furthermore, the rate of accelerated damage due to stress increases with time. Combinations of stress (in corrosion exposure), time, and cycle frequency to produce 15% damage *beyond* that resulting from stressless corrosion are indicated in Figure 11; these data apply to duralumin under tapwater conditions.

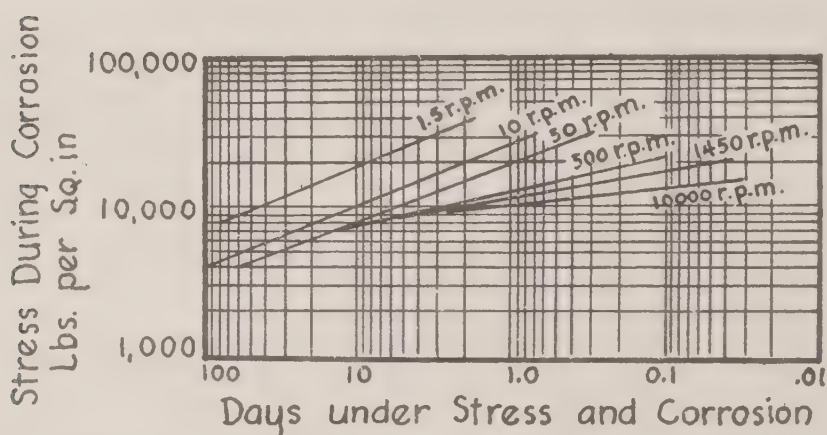


FIGURE 11. Duralumin vs. Fresh Water. Showing Combinations of *Stress*, *Time* and *Rate of Rotation* Resulting in a 15% Drop in Fatigue Limit.

4. Static stress has been found to increase damage slightly to properly treated duralumin in 13 days in a "wet-and-dry" salt water test, as judged by change in tensile properties. In this case the stress applied in exposure was 25,000 lbs. per sq. in. There was no similar effect with Alclad.⁸⁰ Damage to Alclad was plainly evident when the specimens were stressed in an alternating bend test rather than in the static test.

TWO-METAL GALVANIC BEHAVIOR

Aluminum, as we have seen, is one of the least noble metals, yet in spite of this characteristic, it has under many conditions an excellent degree of

corrosion resistance due to the protective oxide. Now the question arises as to what the effect on this protection may be of coupling with more noble metals.

Accelerated attack of a metal through coupling with a more noble metal arises mainly through the fact that there is an increased area of metal on which the cathodic reaction may take place. The increase in anodic attack corresponds roughly with this increase in cathode surface. Actually, in the case of aluminum, another factor enters in by which a solution may have practically no progressive action on the uncoupled metal, yet when coupled with a more noble metal the corrosion is increased out of all proportion to the increase in cathode surface. It would seem that the coupling breaks down the protectiveness of the oxide, so that both the aluminum and the noble metal function as cathodes, the corrosion taking place entirely on the aluminum. It has been shown that with magnesium:noble metal couples exactly this happens.⁵⁷ Under salt water conditions that evolved 13 cc. hydrogen from uncoupled magnesium, from a magnesium:platinum couple 110 cc. gas were evolved at the magnesium and 142 cc. at the platinum.

This same principle seems to apply to aluminum:noble metal couples and it is for this reason, among others, that particular consideration must be given to the possibility of galvanic attack of aluminum.

Broadly speaking, aluminum coupled with a more noble metal—copper, copper alloys, nickel, lead—is ordinarily safe and satisfactory in the less corrosive atmospheres and, for the most part, in non-electrolytes like distilled water and possibly tapwater. In marine atmospheres corrosion of the aluminum at the contact becomes noticeable. In any strong electrolyte, such as acids or salt solutions, corrosion is likely to be too pronounced to make the couples useful. In sea water or brines, for instance, attack is rapid.

Couples exposed for a year to various atmospheres⁴⁹ have given interesting qualitative results. In the most corrosive atmosphere, humid sea-coast air, aluminum suffered accelerated attack in contact with copper, nickel and tin; with zinc the aluminum was perhaps faintly protected, and with iron attack on both the aluminum and the iron was accelerated. In other marine and in industrial atmospheres the galvanic action was less or non-existent, and in rural atmospheres it was non-existent. These results may be taken only as tendencies, in the absence of good quantitative data.

The determinations in Table 10 were made on duralumin:Monel metal couples, the duralumin persisting anodic both in the tap water and in the salt solution.⁵²

The corrosion rates in Table 11 were obtained on duralumin sheet having 1.19 sq. dm. exposed area and carrying in the center a $\frac{3}{8}$ in. Monel metal

TABLE 10.—*Duralumin: Monel Metal Couples vs. Water.*

Hrs.	Min.	Operation	Open Circuit Volts	Short Circuit Amperes
<i>Aerated Tap Water</i>				
0	00	Immerse electrodes	.38	
0	45		.36	
0	46	Close circuit		.0003
0	50			.0002
1	45			.0002
19	35			.0002
19	36	Open circuit	.39	
26	05		.56	
26	06	Close circuit		.0007
26	07			.0003
26	15			.0002
<i>Aerated 3% Sodium Chloride</i>				
0	00	Immerse electrodes		
0	02		.5297	
1	00		.5293	
1	01	Close circuit		.0250
1	03			.0150
2	20			.0128
5	40			.0108
6	00			.0096
22	20			.0043
26	20			.0042
26	25	Open circuit	.4500	
28	50		.5427	
29	50		.4880	
29	51	Close circuit		.0043
46	20	*		.0028

* Anode had developed a thick gelatinous white product with heavy pits beneath.

bolt with a 1 in. square head and a hexagon nut. The solutions were aerated and agitated:

TABLE 11.—*Duralumin: Monel Metal Couple vs. Water.*

		Mg. per sq. dm. per day	
		Uncoupled	Coupled
Tap water—	21 hrs.	+ *	+ *
Sodium chloride—	21 hrs.	+	18 *
	65 hrs.	+ *	24 *
	69 hrs.	16.9	25.7

* Marked pitting occurred on these specimens.

These tests would lead to the conclusion that in sea water the coupling of duralumin with cathodic metals would lead to serious damage, even with small cathode area. In tap water (and similar low conductivity solutions) galvanic acceleration is much less marked and perhaps inconsequential. In one case copper rivets in aluminum in one month tap water exposure resulted in strong attack of the aluminum about the rivet head.⁸⁹ Galvanic coupling with brass¹⁰ caused strong anodic action on aluminum in sea water. Tests with brass and phosphor bronze screws in two casting alloys, in exposure in sea water and in sea air, gave unsatisfactory behavior.⁸

The cathodic and damaging effect of either nickel or chromium plating on aluminum is generally recognized.^{2, 15, 30, 95}

The behavior of iron:aluminum couples seems to be various. Aluminum coupled with iron sometimes has no tendency towards accelerated attack.³⁰ In fact steel may sometimes be anodic to aluminum.^{10, 35} Steel specimens sprayed with aluminum have rusted, in carbonate water, at cracks in the coating, yet in sodium chloride solution the aluminum protected the steel.³⁶ Sterner-Rainer⁹² found steel accelerated action on aluminum alloys in sea water; Seligman and Williams⁸⁹ found the steel to suffer in tapwater, with the aluminum remaining unpitted in over a month's exposure. Bauermeister⁸ found that iron screws in aluminum alloy castings were worse even than brass screws in causing corrosion of the castings, in sea water and sea air.

The polarity of steel:aluminum couples, therefore, is not constant, but depends on the exposure condition and possibly on the nature of the aluminum alloy and its heat treatment.

In Table 12²⁰ are given weight losses of aluminum and of annealed duralumin (unfavorable condition), as obtained in 26-day tests in sea water. The iron certainly was cathodic in these. Further tests were made with various aluminum alloys.²⁰ See Table 13.

TABLE 12.—*Galvanic Couples vs. Sea Water.*

Couple	Weight Change of Aluminum or Duralumin—Units	
	Aluminum	Duralumin
Copper	— 390	— 362
Nickel	— 36	— 46
Iron	— 76	— 150
Cadmium	— 16	+ 10
Zinc	+ 10	+ 37

Zinc as these data indicate, is anodic to aluminum and duralumin.^{1, 2, 30, 95} Experience has shown that couples of light metals with zinc or galvanized steel may be used without particular tendency for either to corrode.³⁰

Cadmium was found anodic to duralumin yet cathodic to aluminum in the tests quoted above, in which the couples were exposed 26 days in sea

TABLE 13.—*Galvanic Couples vs. Sea Water.*

		Weight Change of Aluminum Alloy—Units			
Alloying Element		Copper	Iron	Nickel	Zinc
Silicon	1%	— 112	— 48		+ 25
	2%	— 115	— 50	— 45	+ 19
	5%	— 77	— 22	— 39	+ 20
Manganese	0.5%	— 167	— 12	— 33	+ 14
	2%	— 184	— 5	— 10	+ 17
Magnesium	1%	— 133	— 50	— 38	+ 12
	2%	— 72	— 70	— 31	+ 26

water.²⁰ In other tests as well ^{2, 3} cadmium has been found to be protective, more pronouncedly so with duralumin than with aluminum, and yet cathodic to aluminum ⁹⁵ over a long period of exposure (1 to 2 years) in sea water wet-and-dry and spray tests. Cadmium-plated steel is very commonly, and satisfactorily, used in contact with aluminum and duralumin in airplane construction.

Magnesium is strongly anodic to aluminum. In fact, according to the quantity of hydrogen evolved from couples in exposure to 3% sodium chloride, aluminum is as fully a destructive cathode as copper.⁵⁷

Polarity relationships among the various light metals have been worked out by Edwards and Taylor.³⁰ They have cited a case of severe corrosion of a 5% silicon casting alloy through contact in sea water with a copper content aluminum alloy. In their tests aluminum sheet, of 99.2 to 99.95% purity, was anodic in sodium chloride solutions to duralumin and in most cases to other strong alloys of the heat-treatable type. The potentials between aluminum and duralumin ranged from .041 to .221 volts.

Aluminum is normally slightly anodic to duralumin in dilute electrolytes, a fact of great practical importance. This relationship has led to the product known as Alclad,^{25, 78} which, as already stated, is a bimetal consisting of duralumin with a thin layer of pure aluminum on both sides. With such a product the corrosion, such as it may be, is concentrated on the pure aluminum. Alclad sheet carrying duralumin rivets, and with unprotected cut edges, may be exposed in salt solutions without the danger of damage to the rivets or the duralumin left uncovered at the edges. The bimetal has the strength of the duralumin and yet the better corrosion resistance of pure aluminum.

The same principle has been developed in Europe in the product known as Allautal,⁵⁰ or Duralplat,⁶⁹ both of which are duralumin with outer layers of a strong aluminum alloy that does not carry copper and that, therefore, has better resistance than the duralumin. In this product also the outer layers are anodic and protective to the duralumin. Meissner ⁶⁹ exposed specimens of Duralplat for two years in the North Sea. In the case only of thin specimens, .019 inch in thickness, was there attack of the interior—

ordinary duralumin—sufficient to affect the tensile properties seriously, and with thin sections the entire outer coatings seemed to have been corroded away. In 18 months' exposure on specimens carrying rivets there was no case of rivet loosening. The tensile strength of specimens .039 to .078 inch thick had not suffered and the elongation of .039 inch and .055 inch specimens was unaffected.

PROTECTIVE METHODS

For many purposes the resistance of aluminum and its alloys is of a high order and there is no need of protection by paints or other means. In ordinary atmospheres, or rather in atmospheres that are less corrosive than the more reactive industrial and marine atmospheres, protection is unnecessary. Sometimes paints are applied for the sake of having a painted appearance. Examples of this are various aircraft.

For metal, on the other hand, that is to be exposed to sea water or sea spray, as in the case of seaplanes or on shipboard, some mode of protection is desirable. It is for seaplane construction probably that Alclad was originally developed. This is a very effective method of protection, the principal advantage being that the strength of the construction and the stability of the rivets remain essentially unchanged. Alclad is often painted, sometimes for the sake of appearance but in the more corrosive marine conditions for improving its resistance.

A second method of protection is the anodic oxidation process^{13, 78, 95} by which the thickness of oxide naturally present on aluminum or its alloys is increased perhaps one hundred fold,⁹³ with improvement in its protective value. The first important solution used as a means of producing the coat was chromic acid, the metal being corroded anodically in the bath by an impressed current. The oxide so developed gives good protection, although the subsequent application of paints or lanoline is advantageous.

In this country sulfuric acid²⁷ has lately been displacing chromic in the anodic oxidation process, and in Germany oxalic acid seems to be widely used. All these methods have as the common result, a more protective oxide. It has been stated that anodic coatings are now being applied to much outside architectural work, so that maintenance is practically avoided.²⁷

In the application of paints to the light metals it is extremely important to prepare the surface properly for the priming coat. The anodic oxidation process has been found to be perhaps the best treatment preparatory to painting, the adherence of the paint being better than with a sand-blasted surface or with a surface that has been cleaned, for instance, with benzol. Chemical treatment in a boiling solution of potassium dichromate and sodium carbonate, without anodic treatment, is successful as a preparation for painting.

The common type of failure of painted surfaces is blistering²⁷ due to gas forming faster on the surface of the metal than it can escape through the pores of the paint. Sunlight, or rather ultraviolet light, is particularly damaging to painted surfaces.

Priming coats to be good must be resistant to moisture penetration, they must adhere well and serve as a good base for adherence of subsequent coats, and must carry corrosion-inhibitive pigments. Aluminum paint with a good vehicle may serve both as a priming and a finishing coat. Zinc chromate and certain iron oxide-zinc chromate primers made up in long oil varnish vehicle are widely used. For finishing coats any durable exterior paint or enamel may be used.²⁷

ATMOSPHERE

The reaction between aluminum and oxygen to form the oxide takes place in atmospheric exposure; the coating develops after a shorter or longer time to a thickness and degree of continuity that slows down or, under some conditions, virtually arrests further oxidation. The curves in Figure 12¹⁰⁰ plot the weight increment of freshly surfaced aluminum in exposure in a basement atmosphere, 64° to 67° F.

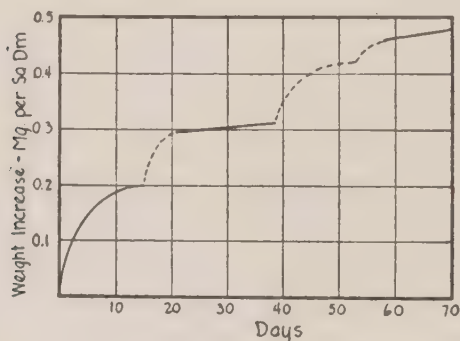


FIGURE 12. Aluminum vs.
Basement Atmosphere.

The irregularities in the curves were believed to be associated with cracking of the oxide layer and subsequent healing. The thickness of the film before the first break in curve B was calculated to be on the order of one millionth of a centimeter. These results are particularly interesting in reflecting the growth of the protective oxide.

The corrosion of aluminum and its alloys depends in part on the humidity and salinity of the atmosphere and the quantity and nature of the impurities in the atmosphere. In dry, clean, inland atmosphere the metals are virtually unaffected; against a moist marine atmosphere they will corrode with a strong tendency to pit; in moist atmosphere carrying dust impurities, pitting may occur. The action may be slow even in conditions considered

severe. Thus aluminum transmission lines installed in 1905 on the shore of the Gulf of Mexico, and in 1911 across salt water in California, remain today in good condition.³¹ Likewise, wire .126 inch in diameter, of 99.55% aluminum exposed on a London roof corroded at an average (weight loss) rate of .4 mg. per sq. dm. per day, over a period of 23 years.¹⁰² The drop over this period, in elastic limit corresponded to the loss in cross section area; the loss in ductility was from an original value of 1.86% to 0.9% (over 13.8 in. length).

Perhaps the most illuminating set of data on the behavior of duralumin in the atmosphere is that of Dix,²⁶ in which the effect on the strength and ductility of sheet and channel sections is determined in exposure to three different atmospheres. On the basis of these tests it may fairly be said, as mentioned by Dix, that the corrosion of properly processed duralumin in the atmosphere is "self-stopping," in the sense that after the first year or two of exposure further damage is virtually halted. The damage that takes place in the first year or two, though it may become serious with the thinner gages, e. g., under .064 inch, may be considered immaterial with heavier metal. The results are given in Table 14.

The same self-stopping nature of the attack of duralumin is illustrated in Figure 13 from tests reported by Rawdon and Mutchler.⁸¹ The curves show the change in elongation of 14 gage duralumin sheet, of proper pre-treatment.

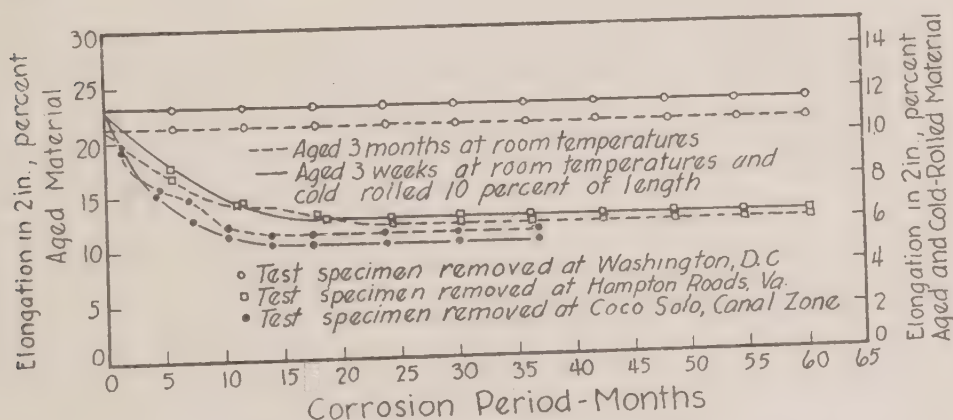


FIGURE 13. Duralumin vs. Weather.

All specimens were given a solution heat-treatment of 15 minutes at 941 degrees Fahrenheit.

Still another example, the metal in this case being 99.55% aluminum wire, 0.125 in. in diameter. The wire was exposed outdoors for 23 years in London, with the following results¹⁰³ shown in Table 15.

TABLE 14.—*Duralumin vs. Atmosphere.*

	Per Cent Drop in Value					
	Industrial			Industrial Marine		Marine
	1 yr.	2 yr.	5 yr.	1 yr.	2 yr.	1 yr. 2 yr.
Heavy section—0.220 in.						
Tensile strength	2			1		2
Yield strength	1			1		1
Elongation	6			6		3
Thin section—.064 in.						
Tensile strength	5	7	7	13	14	5 5
Yield strength	4	7	7	0	5	6 1
Elongation	15	13	15	55	55	30 21

This characteristic that duralumin and aluminum have of resisting progressive corrosion is extremely important to have in mind. It means that the pitting which often is noted on the light metals after atmospheric exposure is truly superficial and remains superficial with prolonged exposure.

TABLE 15.—*Aluminum vs. Atmosphere.*

Year of Test	Breaking Strength Lbs. per sq. in.	Elastic Limit Lbs. per sq. in.	Elongation % in 13.7 in.
1902	28,000	19,200	1.86
1910	24,750	10,700	.95
1925	25,650	11,250	.90

What is the rate of corrosion of aluminum in the atmosphere? We have seen that the rate characteristically slows down with time, so that the rate over any limited exposure period can be considered greater than for a more prolonged period. Wilson's results ¹⁰³ actually indicate that there is a slowing down of rates even after 15 to 20 years. His specific rates for aluminum and various aluminum alloys, based on average weight loss after 23-years exposure to London atmosphere, were 0.4 mg. per sq. dm. per day and le. s. Friend ⁴⁰ determined a rate of less than 0.1 mg. per sq. dm. per day for 7 years in an urban atmosphere.

Rawdon ⁷⁸ has reported the change in strength and ductility of 14 gage duralumin and Alclad specimens exposed 12 to 18 months to temperate sea coast, tropical sea coast and temperate inland atmospheres. The inland atmosphere was least corrosive, the warm coastal most. The Alclad specimens were not appreciably changed in strength or ductility although they were superficially pitted. The properly processed duralumin specimens suffered negligible losses only in the inland exposure. In marine exposure the losses in strength and elongation ranged from negligible to a few per cent only. Even in the cases where there was definite damage, the rate of dam-

age generally slowed down with time, which bears out the findings of Dix, given above. In Rawdon's tests the duralumin specimens as well as the Alclad were superficially pitted. The properly processed duralumin suffered no intercrystalline embrittlement.

Aluminum is in widespread use for exterior and interior architectural work. Outdoors the metal can be expected to last indefinitely, in its cast and relatively heavy wrought and extruded shapes, yet its originally bright surface will not be maintained without periodical cleaning. This latter is particularly true of urban atmospheres, with the accumulation of dust and dirt made more easy by the oxide layer that naturally develops on the metal.

WATERS

Aluminum tanks and piping for storing and handling distilled water are practical; furthermore there is no undesirable contamination of the water derived from the aluminum. In one case²⁹ analysis of water drawn from an aluminum container and piping system yielded less than one part aluminum in one hundred million. The action of natural waters on aluminum is, on the average, low.^{10, 48} A fine white deposit develops on aluminum, yet this does not signify serious weight loss. Soft waters and particularly waters carrying high carbon dioxide appear to be more corrosive than other types. Yet waters softened by zeolite treatment and waters of temporary hardness are usually without much action unless appreciable chlorides and sulfates are also present.³¹ Attack by waters may be more pronounced at the water line. Haase⁴⁵ has described tests, for instance, in which various fresh waters pitted through aluminum containers after 18-days quiet exposure. The metal in this case seems to have carried about 1% iron, probably a deleterious impurity. Bengough and Hudson¹⁰ found no special water line attack of aluminum resulting in several weeks exposure to distilled water, tap water, or sea water that had been boiled to expel dissolved air. Alloys were somewhat attacked.

Chlorides in solution, as already stated, are damaging to the protective oxide layer on aluminum. It is through this fact that sea water with its sodium chloride content of 3%, more or less, often leads to difficulty from corrosion. Sea water is a particularly searching corrosive with the light metals, and brings to light rather effectively the differences in behavior among the different types of aluminum and its alloys. Generally speaking the purer grades of aluminum, the manganese (up to 2%) aluminum alloy and the silicon casting alloys are perhaps the best in behavior. The copper-bearing and the zinc-bearing alloys are inferior. Duralumin is less resistant than pure aluminum, and less resistant than the type of wrought heat-treating alloy that carries 1% silicon and 0.6% magnesium.

Sea water normally pits the aluminum metals, the pits attaining greater depths than those appearing in atmospheric exposure. The rate of pitting attack does not seem to have been worked out for seawater as it has for the atmosphere, and it cannot be said with certainty that the rate slows down with time, although this may be a fact.

In one test a bar of aluminum was exposed three years in water off a dock in Southampton, England. The weight loss was negligible—less than 1 mg. per sq. dm. per day. A layer of protective mud and oil built up on the bar, so that the test was not truly representative.⁴¹

In another test a bar of aluminum was submerged for four years in Bristol, England, Channel.³⁹ The weight loss corrosion rate was 14 mg. per sq. dm. per day, whereas the pitting corrosion rate was about 100 mg. per sq. dm. per day (.05 inch per year). This illustrates how much more corrosive to aluminum sea water is than the normal atmosphere, where average weight loss rates are down well below 1 mg. per sq. dm. per day. It is with these two exposure conditions that the aluminum metals are most concerned, and resistance—in ordinary parlance—is “good” in the atmosphere, and inclined to be “poor” in sea water, relatively speaking, and intermediate in sea spray.

In another set of tests,⁶⁷ specimens of a copper-bearing duralumin, quenched from 932° F. and aged at room temperature, were exposed at part tide level in the North Sea for 3 months. The specimens were .078 inch thick strip. The drop in tensile strength amounted to 6%, and the drop in elongation about 45%. The specimens were pitted, but suffered no intercrystalline attack. Unfortunately the pitting rate was not determined.

Aluminum and aluminum alloys partially immersed in sea water carrying air, for several weeks, in tests by Bengough and Hudson,¹⁰ were very strongly attacked at or just above the water line. Some pitting occurred below the water-line. Actual hydrogen evolution was evident under the microscope. The action was observed to take place as much as one inch above the water-line due to capillary attraction.

SALT SOLUTIONS

Aluminum has good resistance against most aqueous solutions of salts in the neutral range—roughly pH of 7.2 to 6.4. Such salts as sulfates, nitrates, acetates, carbonates, chromates falling within this range have relatively slight action. Neutral chloride solutions are not included in this category for with these, as discussed already in connection with sea water, the protective layer that develops on the aluminum breaks down, or is at least much less protective. As a result aluminum is less satisfactory for handling calcium, sodium, and magnesium brine solutions than for handling

some of the other salt solutions. The action that goes on is both general and of pitting nature, the latter being of course the more serious. Chromate additions to calcium chloride brines slow down considerably the action on aluminum³¹ and make it possible and practical to use aluminum in refrigerating and air-conditioning equipment.

Treble⁹⁷ has suspended aluminum specimens in calcium chloride refrigerating brine in a dairy, the brine carrying customary chromate inhibitor. The rates for commercial aluminum, a 1.15% manganese alloy and a 5% silicon alloy ranged from 0 to 2 mg. per sq. dm. per day, with slight shallow pitting in all cases. Whether the pitting was progressive or not was not noted, although Treble concluded that the metal was safe to use in spite of the pitting.

This relative corrosiveness of chlorides carries on into the alkaline range as well. The alkaline hypochlorites are readily reactive even in very dilute solutions, such for instance as a solution with .02% available chlorine.

Callendar¹⁷ has studied the boundary resistances developing on aluminum in salt solutions and believes the protective effect of chromate and nitrate is due to direct oxidation and that of carbonate due to its effect on precipitating hydroxide. His observations of the effect of nitrate concentration and alloy composition are given below and in Figure 14. The specimens giving the results in Table 16 were submerged in .01% potassium nitrate in tap water.

FIGURE 14. Aluminum vs.
Potassium Nitrate.

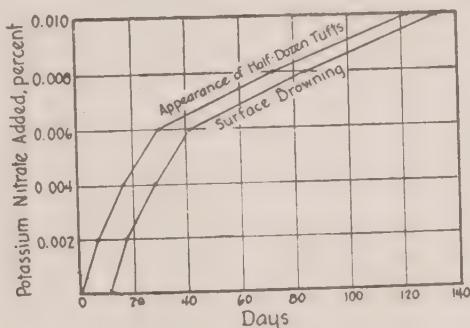


TABLE 16.—Aluminum Alloys vs. Potassium Nitrate.

Fe	Si	Cu	Zn	Mg	Al	Appearance of Corrosion
0.70	0.55	2.94	14.10		Remainder	55 days
0.61	0.40	6.91	1.30		"	136 "
0.75	0.49	11.90			"	65 "
0.42	6.25	0.56		0.13	"	Little in 250 days
0.11	0.11				"	" " 250 "

TABLE 17.—*Aluminum Metals vs. Salt-peroxide Solution*

Alclad				Duralumin				Aluminum			
Thickness mm.	Mg. per sq. dm. per day	Tensile Strength Loss — %	Ductility (elonga- tion) Loss — %	Thickness mm.	Mg. per sq. dm. per day	Tensile Strength Loss — %	Ductility (elonga- tion) Loss — %	Thickness mm.	Mg. per sq. dm. per day	Tensile Strength Loss — %	Ductility (elonga- tion) Loss — %
.8	158	*	*	1.0	250	23	68	.8	.8	*	*
1.6	180	*	*	1.5	180	17	52	1.5	2.6	*	*
2.6	220	*	*	2.0	400	26	79	2.5	2.4	*	*
3.2	200	*	*	4.0	125	2	20	3.0	5.0	*	*

* No certain loss.

A great deal of corrosion testing of the light metals has been done with a solution of sodium chloride and hydrogen peroxide. The presence of hydrogen peroxide in a salt solution is accelerating to corrosion. Since its action is unlike that of practical exposure conditions, and therefore its results perhaps of questionable parallelism with practical exposure conditions, only one set of data will be offered here. These tests⁷³ point out particularly the lower degree of attack of pure aluminum, acceleration of the attack of aluminum by coupling with duralumin in the product Alclad, the destructive nature of the attack on duralumin, and the prevention of this attack by coupling with pure aluminum.

Exposed 5 days in a mixture of 3% sodium chloride and .1% hydrogen peroxide at 68° F. and under constant agitation, damage was experienced as shown in Table 17. In the case of the Alclad specimens the duralumin was exposed at cut edges. Corrosion of these specimens was confined to the outer layers of pure aluminum. The pre-treatment of the duralumin was not described in the paper in which these results appeared.

A similar study was made of the effect of a salt water spray test of 66-days duration. This proved to be far less damaging on the basis of weight loss rates, yet was fully as damaging to the strength and ductility of the duralumin specimens.

Following are given data on the effect of a number of salt solutions of the neutral and relatively weakly corrosive type on aluminum. Included are data on chloride solutions. Reference was not made by the authors of

TABLE 18.—*Aluminum vs. Salt Solutions.*

Method	Mg. per sq. dm. per day	
	Sodium Chloride 1 N	Potassium Dichromate 1 N
Total immersion		
Air-agitated	2.2	1
Quiet	4	1.5
Alternate immersion		
Continuous	1.5	.7
Intermittent4	1.5
Spray (30 days)4	.1

the papers from which these data have been taken to possible pitting action.

The rates in Table 18 were obtained at room temperature in 48 hours following previous 48-hour exposure.⁴²

In the tests in Table 19 specimens were immersed in quiet salt solutions for 7 days at 64° to 68° F.—the solution being renewed daily—and for 28 days, respectively.⁴⁶

TABLE 19.—*Aluminum vs. Salt Solutions.*

	Conc. %	Mg. per sq. dm. per day	
		7 days	28 days
Magnesium chloride9	23	4.6
Calcium chloride	1.1	7	1
Sodium chloride	1.3	<1	.3
Sodium carbonate	1.0	110	5

Thirty day submersion at room temperature gave the data in Table 20.⁴⁷

TABLE 20.—*Aluminum Metals vs. Salt Solutions*

	Mg. per sq. dm. per day	
	Aluminum	Duralumin
Ammonium chloride—5%	4	4
Magnesium chloride—1%7	.7
Sodium sulfate—10%	*	*
Magnesium sulfate—5%3	.3

* No determinable weight loss.

Immersion of aluminum for 14 days at 140° to 158° F. in 1 to 75% sodium sulfate solutions gave rates of 3.6 mg. per sq. dm. per day and less.⁴ Exposure to air-saturated 4% magnesium sulfate at 140° to 176° F. for 14 days gave a rate of less than 1 mg. per sq. dm. per day for aluminum.

Aluminum exposed 150 hours to ammonia salt solutions, dilute to concentrated, gave the data in Table 21.

TABLE 21.—*Aluminum vs. Ammonium Salts.*

		Mg. per sq. dm. per day	
		68° F.	140°-158° F.
Ammonium carbonate		<1	<1
" chloride		1.5- $\frac{1}{2}$	5-1
" sulfate		<1	1.1- $\frac{1}{2}$
" nitrate		0	0

Solutions of salts of heavy metals, such as ferric sulfate and chloride, stannic chloride, mercuric chloride, copper sulfate, silver nitrate, are strongly corrosive to aluminum both because of acid character and oxidizing capacity. In no case is it feasible to use aluminum for handling these.

Salt solutions reacting alkaline, such as the alkali carbonates, phosphates, hypochlorites are too readily reactive in the absence of inhibitor, to make the use of aluminum with these practical for most purposes. As already stated, the addition of inhibitors to such solutions is beneficial, and makes the use of many cleaners carrying these substances practical.

FOOD PRODUCTS ⁵

Aluminum is very extensively used with foodstuffs, both as ordinary household cooking utensils and as equipment in the processing and handling

of foods in the dairy, the canning plant, and so on. The resistance of aluminum to corrosion by foodstuffs is of a high order—with the more acid products less than with the neutral products—, and aluminum has the further advantage that its compounds are colorless. Finally, aluminum in the quantities normally picked up by foodstuffs is non-toxic.

Unsatisfactory features of aluminum at times are a tendency to pit, softness, the difficulty in some cases with which it is kept clean, poor resistance to alkaline solutions. Alkaline cleaning compounds must carry inhibitors in order that undue action on the aluminum may not take place.

Actual corrosion rates of aluminum in contact with food products, other than the more acid fruit juices, range for the most part, expressed as mg. per sq. dm. per day, from virtually zero to perhaps 5 or 10. Action as slight as this is of course negligible when viewed from any angle—life of the metal, toxicity, contamination of the product. Foodstuffs normally are held for short periods of time only in metal processing and handling equipment. Consequently, with such low rates of attack, a content of dissolved metal has no time to build up in the product.

A great many foodstuffs are cooked in the household in the presence of salt, or sodium chloride. It has already been pointed out that this substance, among the neutral solutions, is particularly corrosive to aluminum. The fact is seldom if ever important when considering the suitability of aluminum cooking utensils. Even though corrosion may be somewhat greater when cooking such a product, the time of contact is so short and the actual corrosion rate still sufficiently low that trouble is not experienced. It is another matter, however, to consider aluminum suitable for handling the brine solutions found in canneries. It is only where inhibitors may be added to brines that aluminum may be used at all.

With respect to the non-toxic quality of aluminum, it really is sufficient to say—to lay the ghost of toxicity that has in the past been raised—that

TABLE 22.—*Aluminum Pick-up by Foods.*

Foodstuff	Duration of cooking — Minutes	Aluminum content		Increase in Aluminum p.p.m.
		Glass p.p.m.	Aluminum p.p.m.	
Fried bacon	5	.25	.68	.43
Boiled ham	120	.64	.87	.23
Percolated coffee	15	.25	1.03	.78
Oatmeal	150	1.43	8.28	6.85
Stewed tomatoes	20	.12	4.20	4.08
Creamed cabbage				
cooked with soda	45	.34	90.8	90.5
cooked without soda	45	.37	2.76	2.39
Rhubarb	5	.95	13.45	12.5
Prunes	40	4.60	7.10	2.5
Apple butter	390	5.28	118	113*

*Includes time to concentrate cider.

aluminum is a normal constituent of foodstuffs, and that the further quantities absorbed from the utensil in normal use are not significant. Some excellently illustrative data have been obtained in cooking tests using glass utensils in comparison with aluminum utensils.⁹ A selection from the data is given in Table 22.

The question as to whether or not aluminum is damaging when taken into the human system has been considered by innumerable investigators. The considered opinion of scientific authority is in agreement that aluminum in the amounts absorbed with food products is perfectly harmless. Perhaps the best statement is that of the Bureau of Standards³:

"The Bureau often receives inquiries relative to the toxic properties of aluminum, particularly in reference to its use as a cooking utensil. The following opinion was expressed by the Public Health Service concerning this matter: 'There is no evidence available which would indicate that aluminum cooking utensils represent a potential danger to health. There is no question that if strongly acid or alkaline foods are prepared in such containers a certain amount of the metal will be dissolved and will pass over into the food. It is very doubtful, however, whether a sufficient amount of metal will be found under such circumstances in food so as to produce a deleterious effect on the health of persons consuming this food. It should be remembered that certain widely used baking powders contain considerable quantities of aluminum salts and while certain objections have been raised to the use of these aluminum baking powders, the question of their injuriousness has not been definitely established. In the use of aluminum cooking utensils it may, perhaps, be advisable to avoid strongly acid foods. It may also be desirable not to let food stand for many hours in the aluminum cooking utensils.'"

Cold fruit juices are reasonably well resisted by aluminum, though the action is inclined to be somewhat more rapid than that of less acid food products. Hot fruit juices on the other hand become rather seriously corrosive. Specimens of metal were exposed in reflux condensers to boiling juices⁷¹ with the results shown in Table 23.

TABLE 23.—*Aluminum vs. Boiling Fruit Juices.*

	Mg. per sq. dm. per day	
	5 Hours	24 Hours
Tomato juice—.486% acidity	18	
Apple juice—.28% acidity	70	54
Red grape juice—.75% acidity	45	41
Lemon juice—.52% acidity	138	140

Blount and Bailey¹² have remarked that aluminum kettles and juice pans handling orange juice after a year's use required removing due to pitting. They made tests in boiling juice within a reflux condenser, over a 24-hour period following 72-hours previous exposure. See Table 24.

Aluminum is very successfully used handling milk products, in all varieties of equipment. The resistance of aluminum to milk is high, once the simple precaution is taken to avoid coupling the metal with other, more

TABLE 24.—*Aluminum vs. Boiling Orange Juice.*

	Mg. per sq. dm. per day
Aluminum	75
Aluminum (1½% manganese)	95

noble metals such as copper and the bronzes. A great deal of corrosion testing has been done; perhaps the best set of data is that given by Trebler.⁹⁷ He suspended strips of the various aluminum metals at various places in operating pasteurizing equipment during one day's run of 8 hours. The corrosion rates in Table 25 resulted.

TABLE 25.—*Aluminum vs. Milk.*

Location	Mg. per sq. dm. per day		
	Commercial Aluminum	Aluminum with 1.15% Manganese	5% Silicon Casting Alloy
Regenerator, bottom inside	5	19	12
“ middle inside		8	3
“ top inside	3	5	8
Electropure outlet pipe	+	+	+
“ “ “	+	+	+
Regenerator, top outside	40	37	
“ middle outside	3	5	
“ bottom outside	5	6	
Cooler, outside	5	3	

Specimens of the same metals were suspended in buttermilk during one cycle of operation. During the cycle freshly separated skimmed milk was run into the vat at 80° to 90° F. and the temperature then raised in about one hour to 180° to 190° F. and maintained at this temperature for 30 minutes. The milk was cooled to 70° F. and the starter added and then left at this temperature for 15 hours. The curd was then broken and the buttermilk cooled to 40° F. The corrosion rates ranged from 6 to less than 1 mg. per sq. dm. per day.

These rates indicate very well the low order of attack to be expected.

ACID SOLUTIONS

Aluminum is used successfully for handling a good many acid conditions. In acid solutions the behavior of the metal depends on the behavior of the protective oxide. In concentrated nitric acid and in acetic acid of all concentrations the resistance is good. In many exposures of the organic acids the metal is also used. Sulphuric, dilute nitric, phosphoric and particularly hydrochloric are corrosive. Increasing hydrogen-ion concentration favors corrosion, in the sense that solutions of higher hydrogen-ion concentration,

no matter what the acid, are corrosive, and solutions of lower hydrogen-ion concentration, no matter what the acid, are resisted fairly well or better. An exception to this generalization is that hydrochloric acid even in very dilute solutions is corrosive.

The conflicting factors, therefore, seem to be hydrogen-ion concentration as the agency promoting corrosion and oxide-forming capacity as the preventive. Acid that gains access to fresh unoxidized aluminum is rapidly reactive, the action being accompanied by strong hydrogen evolution. This latter fact is not true of the acid attack of the more noble metals like copper and nickel which require the presence of oxygen as a depolarizer in order that corrosion may continue. The part that oxygen plays in the corrosion of aluminum, therefore, is quite unlike its role with copper, since in the case of aluminum the oxygen does not act appreciably as an accelerant by depolarizing hydrogen. Dissolved oxygen does not appear to be necessary for the formation and maintenance of the protective film.

The pure grades of commercial aluminum, and the stronger manganese alloys are the types used for handling acids. Duralumin, and the various more highly alloyed casting compositions are little used with them.

Acid solutions carrying other more noble metals in solution—such as copper or iron or tin or mercury—cannot be used with aluminum. Such substances are strongly corrosive.

The test results of Whitman and Russell¹⁰¹ indicate the relatively negligible effect of oxygen on the acid corrosion of aluminum. Slight acceleration with oxygen saturation occurred in some solutions, deceleration in others. The tests ran 5 hours at 68° F. It is presumed that the oxide film was present and maintained on the metal in the hydrogen-saturated acetic solutions. See Table 26. Acetic is seen to be only weakly corrosive, hydrochloric very strongly so and sulfuric intermediate.

TABLE 26.—*Aluminum vs. Acids.*

		Mg. per sq. dm. per day	
		Hydrogen Sat'd	Oxygen Sat'd
Sulfuric	6%	18	62
	50%	126	111
	96.5%	250	210
Hydrochloric	4%	19,800	60,000
Nitric	3%	49	86
	30%	175	148
	70%	114	100
Acetic	6%	3.7	9.5
	50%	<1	5.6
	glacial	11	11

The effect of aeration was likewise studied in the tests described below,⁴² and incidentally, found to be less important than with other

metals tested at the same time. The rates in acetic were low, and comparable to those of Whitman and Russell.¹⁰¹ The tests ran 48 hours following previous 48-hours exposure, at room temperature. See Table 27.

TABLE 27.—*Aluminum vs. Acids.*

	Mg. per sq. dm. per day	
	Hydrochloric 1 N	Acetic 1 N
Total immersion		
Quiet	450	5.2
Air-agitated	1050	5.2
Alternate immersion		
Continuous	2200	8.8
Intermittent	620	7.1
Spray (30 days)	80	20

Duralumin (heat-treatment not known) was more corroded than aluminum in most of the solutions of Hatfield's quiet submersion, room temperature tests.⁴⁷ The sulfuric and nitric rates for aluminum were moderate to light, the rates in the 30-day organic acid tests were low. See Table 28.

TABLE 28.—*Aluminum Metals vs. Acids*

		Mg. per sq. dm. per day	
		Aluminum	Duralumin
<i>24-hour duration</i>			
Hydrochloric	3.6%	2680	6560
	conc.	8410	43,590
Nitric	6.3%	40	270
	32%	90	250
Sulfuric	5%	20	60
	10%	20	40
<i>30-day duration</i>			
Acetic	33%	2	6
Citric	5%	.3	.3
Vinegar		2	2.6

Of the rates in Table 29⁴⁶ those in 4-hour exposure are much higher than those in longer exposure. It is the nature of metals that develop protective films to corrode at rates decreasing with time. With nitric and sulfuric, a protective coating obviously develops on aluminum, with hydrochloric it does not, insofar as these test conditions apply.

TABLE 29.—*Aluminum vs. Acids.*

		Mg. per sq. dm. per day		
		4 Hours	7 Days*	28 Days
	%			
	Conc.			
Nitric	1.2	120	14	20
Hydrochloric72	60	50	60
Sulfuric98	300	13	10

* Solution renewed daily.

The rates in Table 30²⁴ are low to moderate. The solutions were held at 110° to 120° F., and the duration was 7 days.

TABLE 30.—*Aluminum vs. Acids.*

	Mg. per sq. dm. per day
Nitric—5%	33
Sulfuric—5%	134

The action of the warm to hot dilute organic acids in Table 31, over a period of 24 to 29 hours, was moderate.⁷¹

TABLE 31.—*Aluminum vs. Acids.*

	Temp.	Mg. per sq. dm. per day
Citric — .97%	150° F.	24
Tartaric — 1.12%	boiling	46
Malic — .97%	boiling	22
Acetic — .9%	boiling	27

In the tests described in Table 32, the action at room temperature of quiet organic acids was negligible to low; the very great accelerating effect

TABLE 32.—*Aluminum vs. Acids.*

	Temp. ° F.	Duration	Mg. per sq. dm. per day
Hydrochloric 1%	70	5 days	223
Sulfuric 1%	70	5 days	9.8
Acetic 1%	70	5 days	.27
Butyric 1%	70	5 days	1.2
Lactic 1%	70	5 days	.22
Citric 0.2%	70	5 days	+
Butyric 1%	145	5 hrs.	74
Lactic 1%	145	5 hrs.	50

of higher temperatures in the case of butyric and lactic is notable.⁵¹ The specimens were partially immersed in sealed containers.

Hydrochloric. Hydrochloric acid, as the results that have already been given show, is very actively corrosive to aluminum. The failure of the oxide to be protective may be attributed to its solubility in hydrochloric acid and to the penetrating capacity of the chloride ion. The action of hydrochloric on aluminum is accompanied by strong hydrogen evolution, which likewise is an obstacle to the formation of a protective layer. Maass and Wiederholt⁶⁶ exposed various light alloy compositions, ranging from 99 to 80% aluminum, to dilute hydrochloric for a 5-month period with the following results:

	Mg. per sq. dm. per day
Hydrochloric—0.5 normal	30–110
Hydrochloric—0.05 normal	7–40

Edwards²⁸ is authority for the statement that a specimen of aluminum of very high purity showed no appreciable corrosion after 6-weeks exposure in fairly dilute hydrochloric.

From the practical standpoint, aluminum cannot be used with hydrochloric acid solutions of any concentration.

Sulfuric. In sulfuric acid aluminum is corroded at rates ranging from low, in quiet long-time exposure in dilute solutions, to moderate and high at elevated temperatures and in stronger acid concentrations. The bounds within which a low degree of attack may be expected are not clearly marked. In addition to the data on sulfuric already quoted, the data in Table 33 are given to outline the effect of temperature and of concentration.¹⁰¹ The duration was 5 hours.

TABLE 33.—*Aluminum vs. Sulfuric Acid.*

Conc. %	Temp. ° F.	Mg. per sq. dm. per day	
		Hydrogen Stream	Oxygen Stream
6	68	18	62
	95	34	110
	122	195	346
50	68	116	110
	95	364	430
	122	1,230	1,660
96.5	68	250	210
	95	820	870
	122	3,300	3,300

The rates of attack in room temperature 25-hour tests by Calcott and Whetzel¹⁶ were severe. (See Table 34.)

TABLE 34.—*Aluminum vs. Sulfuric Acid.*

Conc. %	Mg. per sq. dm. per day	Conc. %	Mg. per sq. dm. per day
5	158	30	380
10	292	40	450
20	225	50	880

Ferric iron in sulfuric acid is corrosive, even with relatively low contents of acid and iron. In the tests below the attack in every case was of a pitting nature.⁹¹ The specimens were exposed to flowing mine water for from 16 to 120 days.

TABLE 35.—*Aluminum vs. Sulfuric Acid with Ferric Salt.*

	Sulfuric acid—%	.14	.22	.04
	Ferric iron —%	.006	.09	.014
	Mg. per sq. dm. per day			
Aluminum	84	155	42	
95% Aluminum 5% silicon, cast	242	220	43	
98% Aluminum 2% manganese, cast	84	223	39	
Aluminum alloy, rolled	59	176	38	
Aluminum-manganese alloy, rolled	159	203	45	

Nitric. Aluminum has been used on a wide scale in handling nitric acid solutions ⁸⁶ for such purposes as containers and pipe lines and, in the case of concentrated acid, for shipping drums. In fact, it is the only metal approved by the Interstate Commerce Commission for shipment containers of nitric acid over 80% in strength.

Chlorides and sulfates present in nitric increase corrosion very materially. It is only where these are absent or of very low concentration that aluminum equipment will have satisfactory behavior.

Supplementary data on the effect of nitric acid are given in Table 36.

TABLE 36.—*Aluminum vs. Nitric Acid.*

Conc. %	Temp. ° F.	Mg. per sq. dm. per day
15	68	340
	162	2,400
50	68	220
	122	1,900
	162	3,200

The tests ⁴ in Table 37 were made with nitric, and nitric and sulfuric mixtures.

TABLE 37.—*Aluminum vs. Nitric-Sulfuric Acid.*

		Mg. per sq. dm. per day
Nitric—7 parts to 3 of water		
68° F.	— 96 hours	82
140°–158° F.	— 96 hours	1,320
Nitric—1 part to 2 parts sulfuric		
68° F.	— 50 hours	290
167° F.	— 1 hour	38,000
Nitric—2 parts to 1 part sulfuric		
68° F.	— 50 hours	180
167° F.	— 1 hour	24,000

Sulfurous. Though aluminum is generally a good resistant to sulfidizing conditions, the attack of sulfurous acid is rather strong. Simple immersion exposure for instance will result in evident corrosion. Moist sulfur dioxide gases at elevated temperatures sometimes may be handled with aluminum. The only available sulfurous corrosion rate is that from tests ⁵⁸ in a solution carrying calcium bisulfite and 4.5% free sulfurous acid. The tests were made at 275° F., with an average pressure of 130 lbs., for 7 hours. The average corrosion rate for 14 specimens was 5,300 mg. per sq. dm. per day. This of course has no relation whatsoever to behavior at ordinary temperatures.

Chromic. Aluminum is only moderately corroded by chromic acid, as the rates given in Table 38 will testify.⁴ The tests ran 150 hours.

TABLE 38.—*Aluminum vs. Chromic Acid.*

Conc. %	Mg. per sq. dm. per day	
	68° F.	140°–158° F.
1	4	5
5	15	21
10	21	44
Conc.	68	260

Phosphoric. Phosphoric acid solutions attack aluminum moderately⁴; the rates in Table 39 were obtained in 14-day tests. Kosting and Heins⁵⁵ have given rates of several thousand mg. per sq. dm. per day in moderately high concentrations, at ordinary temperatures and hot.

TABLE 39.—*Aluminum vs. Phosphoric Acid.*

Conc. %	Mg. per sq. dm. per day	
	68° F.	140°–158° F.
1	4	6
5	18	46
10	38	93
20	63	100

Acetic. Acetic acid is very widely handled with aluminum. Corrosion rates of 4 to 25 mg. per sq. dm. per day seem characteristic for concentrations of 1 to 10 per cent in the cold, stronger and weaker solutions being no more corrosive, usually less. The presence of certain impurities, as chlorides, hastens attack. Higher temperatures are rather strongly accelerating.

The rates in Table 40 were obtained in 24-hour, room temperature tests in air-saturated acetic.⁵² These rates are without doubt higher than rates

TABLE 40.—*Aluminum vs. Acetic Acid.*

Conc. %	Mg. per sq. dm. per day
1	36
5	84
10	29
20	32
50	46
glacial	10.7

that might have obtained if the tests had run for a longer period. A number of sets of data have already been given, showing much lower rates in acetic; these are believed more accurate indications.

The rates in acid at room temperature are negligible; in boiling dilute acid the rates are high.⁴ (See Table 41.)

TABLE 41.—*Aluminum vs. Acetic Acid.*

Conc. %	Mg. per sq. dm. per day	
	68° F.—4 Wks.	Boiling—24 Hrs.
1	< 1	1,200
25	< 1	390
85	< 1	150
90	< 1	75
95	< 1	39

The rates in Table 42⁵³ in boiling acid are likewise high in the dilute concentrations. The lessening of rates with higher concentrations is important to note, for with hot concentrated acid aluminum is used rather widely. These tests also ran 24 hours:

TABLE 42.—*Aluminum vs. Boiling Acetic Acid.*

Conc. %	Mg. per sq. dm. per day	Conc. %	Mg. per sq. dm. per day
1	589	60	205
3	750	70	120
5	420	85	80
10	340	glacial	14
50	340		

Seligman and Williams⁸⁷ found acetic at room temperature, in concentrations from 99 to less than one per cent, to range around 1 mg. per sq. dm. per day in quiet exposure; but⁸⁵ boiling acid was found to be much more corrosive. The boiling acid tests giving the rates in Table 43 ran 4

TABLE 43.—*Aluminum vs. Boiling Acetic Acid.*

Conc. %	Mg. per sq. dm. per day
50	315
60	285
70	240
80	210
90	100
98	33
99.9	3

hours. These investigators found also that dehydrated hot acetic acid was extremely corrosive to aluminum. They have summarized their observations: "For acetic, propionic, and butyric acids of high concentration, aluminum plant should have a reasonable life so long as there is no possibility of the formation of the anhydrous acids. Wherever these can be produced, as for instance by heating acetic acid with acetic anhydride or where efficient dephlegmating arrangements are in use, the vessels are likely to be

very seriously attacked, unless small quantities of water can be introduced at the threatened points. Aluminum plant is not likely to have a prolonged life where it is in contact with hot acids of lower concentration."

Tests made on aluminum in actual processing solutions in a chemical plant have given the following results ⁵²:

Crude 80% acetic, specimens submerged near the bottom of a storage tank for 4 days—12. mg. per sq. dm. per day.

Commercially pure 80% acetic, specimens submerged at the bottom of a storage tank, for 14 days at room temperature—16 mg. per sq. dm. per day.

Commercially pure 80% acetic, specimens partially immersed in a storage tank for 6 days at room temperature—1000 mg. per sq. dm. per day.

The strong attack of the partially immersed specimens is remarkable.

Other organic acids. Other organic acids—citric, malic, lactic, tartaric, oxalic, etc.—seem to be somewhat more corrosive to aluminum than acetic, yet, judging by the data already quoted, these may be reasonably well resisted in the cold. The hot acids are moderately to strongly corrosive. The tests in Table 44 ran 7 to 14 days ⁴:

TABLE 44.—*Aluminum vs. Acids.*

		Mg. per sq. dm. per day	
		Room Temp.	Hot (140°-176° F.)
Oxalic	— .4%	4	
	.5	4	5
	2	9	31
	5	8	86
	10	9	98
Lactic	— 1	5	33
	5	5	20
	10	5	21
Salicylic	— 1		6
	2		13
Phenols	— 1		< 1
	3		< 1
	10		< 1
	50		1
	75		< 1
	75		20*

* 194-212° F.

Rates obtained in plant tests in process solutions ⁵² were as follows. These are to be compared with rates already given for acetic acid under rather similar conditions.

Formic acid

Exposed in a still treating 90% acid at 212° F., for 8 days—530 mg. per sq. dm. per day.

Exposed in the vapor of the still, for 27 days—200 mg. per sq. dm. per day.

At bottom of storage tank holding 90% acid at room temperature, for 138 days—76 mg. per sq. dm. per day.

For 6 days partially immersed in 90% acid at room temperature—2000 mg. per sq. dm. per day.

Lactic acid

Immersed 17 days in tank receiving condensate (spent liquor) from still handling impure 30% lactic at 80°–150° F.—150 mg. per sq. dm. per day.

Partially immersed for 8 days in the same—500 mg. per sq. dm. per day.

In a still concentrating lactic from 5 to 48% under vacuum—280 mg. per sq. dm. per day.

Boiling propionic and butyric acids, and other acids of the series, were found to be extremely corrosive when dehydrated.⁸⁵ As an illustration the data in Table 45 are quoted for boiling propionic.

TABLE 45.—*Aluminum vs. Boiling Propionic Acid.*

Conc. %	Time	Mg. per sq. dm. per day
80	4 hrs.	265
98–99	5 hrs.	5
Dehydrated	30 min.	200,000

ALKALINE SOLUTIONS

Since aluminum oxide is soluble in caustic alkaline solutions, these readily attack aluminum. Thus sodium and potassium hydroxide, sodium carbonate and bicarbonate, tri-sodium phosphate, and other products, without inhibitor addition²² cannot be handled with aluminum. Even the alkali present in ordinary household cleaning mixtures is sufficient to have serious effect unless these carry an inhibitor. Hard soaps do not corrode, soft soaps corrode vigorously.³¹

It has been found that the presence of sodium silicate in caustic solutions decreases and in some cases actually prevents this attack. Certain minimum ratios of silicate to caustic are necessary for protection. The addition of 1% silicate to a 5% sodium carbonate solution was effective in one case. The silicate present in laundry soaps prevents the relatively rapid destruction of household washing machines by the alkali of the soaps. Other inhibitors used are chromates and dichromates. Tests have been made by Rohrig⁸² on the effectiveness of an addition of 0.75% sodium silicate, in 30 minute exposure, an important comparison being given in Table 46.

TABLE 46.—*Aluminum vs. Alkaline Solutions.*

	Mg. per sq. dm. per day	
	Without Silicate	With Silicate
Sodium hydroxide 10%—68° F. . .	15,000	17,000
Sodium carbonate 10%—149° F. .	4,600	< 5

Ammonium hydroxide solutions on the other hand are generally well resisted by aluminum. Aluminum is used in connection with ammonia refrigerating systems and ammonia recovery equipment. Rawdon ⁷⁵ found ammonia and ammonium chloride mixtures to be very corrosive, whereas ammonium hydroxide alone was well resisted.

Data ⁴² on both caustic and ammonia solutions are given in Table 47. That the action of ammonia solutions may sometimes be moderately severe is indicated. The tests ran for 48 hours following a previous 48-hour exposure, at room temperature.

TABLE 47.—*Aluminum vs. Alkaline Solutions.*

Method	Mg. per sq. dm. per day	
	Sodium Hydroxide	Ammonium Hydroxide
	1 N	1 N
Total immersion		
Quiet	26,000	<.1; 60
Air-agitated	26,000	<.1; 40
Alternate immersion		
Continuous	6,000	88
Intermittent	1,300	17
Spray (30 days)	15	.7

Under simple immersion conditions in 33% sodium hydroxide, for 30 days at room temperature, both aluminum and duralumin corroded at rates over 2,000 mg. per sq. dm. per day.⁴⁷

In one-fifth normal solution under simple immersion conditions at room temperature the rates in Table 48 were obtained.⁴⁶

TABLE 48.—*Aluminum vs. Alkaline Solutions.*

	Mg. per sq. dm. per day	
	7 Days	28 Days
Sodium hydroxide	2,900	95
Ammonium hydroxide	50	.7

The rates in Table 49 were obtained in 14-day tests.⁴

TABLE 49.—*Aluminum vs. Aqueous Ammonia.*

Conditions	Mg. per sq. dm. per day
Submerged in freshly produced aqueous ammonia mixed with tar	7
Submerged in solution carrying 1.7% ammonia	4
Submerged in solution carrying 1% ammonia	17
Hung in vapor of fresh ammonia	< 1

Tests giving the results in Table 50 ran 50 hours at 68° F.⁴

TABLE 50.—*Aluminum vs. Aqueous Ammonia.*

Conc. %	Mg. per sq. dm. per day
1	1.5
5	4.1
10	4.8
Conc.	7.2

HIGH TEMPERATURES

The limitations in the high temperature utility of aluminum and the light alloys lie more in mechanical deficiency than in chemical. The oxide film developing under heat is highly protective.⁷² See Figure 15. The thickness of the film in this case was calculated to be .00002 cm. (.000008 in.), assuming normal density. The appearance of the metal at the end of 890 hours was "distinctly chalk white."

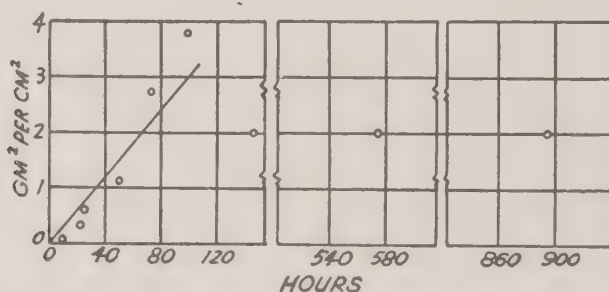


FIGURE 15. Oxidation of Aluminum at 1112° F.

Aluminum furthermore does not deteriorate, as the copper and nickel metals do, in hot sulfur-bearing gases. This property is utilized to some extent in petroleum refineries where the strength of hot aluminum is sufficient and where chloride corrosion is not encountered.

Aluminum metals also are limited in the handling of steam by their softness and low strength. The corrosive action of steam may be very slight. In one case⁹⁰ refined aluminum held in dry steam, under pressure, at 572° F. for 215 hours was without change in appearance or weight. Sheet of ordinary aluminum held 100 hours in super-heated steam at 932° F. acquired a few blisters.

An interesting set of data on the effect of steam is given in Table 51. Super-heated steam was passed at 120 to 140 ft. per sec., parallel to the surface of the metal, for 34 days—9 hours each day—at 570° to 660° F. The specimens were 1.2 in. square with a .32-inch diameter hole in the

center. The attack on the pure aluminum was not erosive, since it occurred as well in quiet steam.

TABLE 51.—*Aluminum Alloys vs. Super-heated Steam.*

Thickness In.	Alloy	Weight Increase Grams
.06	Very pure aluminum 99.87 Al	completely destroyed
.06	Rolled aluminum .47 Si .72 Fe	.074
.18	Rolled aluminum .37 Si .77 Fe	.766
.18	Cast aluminum .42 Si .83 Fe	.127
.18	8% Cu .45 Si .87 Fe 7.8 Cu	.321
.14	Cast duralumin 4 Cu .5 Mg .5 Mn	.236
.18	Cast alpax 13 Si .63 Fe	.069

ALUMINUM

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Chapter VII

Zinc and Zinc Coatings

The basis of the greater use of zinc as a corrosion-resistant metal is the comparative stability both of zinc coatings on steel and of solid zinc sheet in exposure to the atmosphere and of zinc coatings to natural waters and sea water.^{2, 3, 51} Zinc-coated sheet is commonly used in general building construction; zinc-coated pipe and pipe fittings in domestic and industrial water supply systems; zinc-coated wire for fencing and screening; and zinc-coated hardware practically universally. Solid zinc sheet is a roofing material, one of several applications in which the good ductility and malleability and the low strength of zinc allow forming into shapes. The structural strength of solid zinc is too low to make it a generally useful engineering metal.

TYPES OF ZINC COATINGS

Zinc-coating²⁶ is accomplished by three methods, each with its distinctive limitations and utility. The oldest method—and that used largely at the present time—is the hot-dip galvanizing process. In this, iron or steel, cleaned by acid pickling, is passed through a flux and into a bath of molten zinc at a temperature of about 820° to 830° F.; the resulting coat consists of an outer layer of zinc of the same purity as the bath, underlain by a series of zinc-iron alloys. The adherence to the base metal is good but variations in the purity of the zinc, composition of the base, and operating conditions greatly affect the tendency to cracking of the coating when the article is subjected to bending. The surface of the coating is slightly uneven and has the well-recognized spangled appearance. The short exposure to heat involved in the galvanizing process does not materially modify the mechanical properties of even cold-drawn steel spring wire, as is shown by the fact that wire for suspension bridge cable has carried, after galvanizing, a tensile strength of 200,000 pounds per square inch.

“Sherardizing” is a dry zinc-coating process; iron and steel objects are packed in zinc dust, containing some zinc oxide, and heated to 480° to 750° F. The result is a coating of zinc-iron alloys, thinner than ordinarily obtained in the hot-dip process and of good adherence though subject to

dusting if bent. The process requires a good deal of care as to temperature control and impurities to give good results. Thick-walled and complicated objects, not of the larger sizes, are adaptable, and the general ease of processing makes the method economical in small-scale work. The time of exposure to heat is sufficient to modify the mechanical properties of some steels.

Zinc electroplating differs from the other methods mainly in the absence of iron-zinc alloys in the coating and in the fact that ordinary temperatures only are involved. Uniform, thin and smooth coatings are characteristic though new processes for the production of heavy coatings have been developed. Uniformly good bending properties are probably more easily attained with this process than with the others. All galvanized coatings can be soldered.

The spray gun in applying zinc is specially adapted to coating immobile surfaces such as tanks and exposed structural steel. A coating of any thickness may be obtained, but the process is fairly costly.

GENERAL CORROSION RESISTANCE

The sphere of zinc as a corrosion-resisting metal, as already stated, is largely confined to the action of the atmosphere and various types of waters. In the protection of iron from rusting, zinc-coating is in general more satisfactory than painting, tinning or the application of other metal coatings. Zinc not only protects the underlying iron, but also, by virtue of its electrochemical nature, definitely and characteristically protects iron where exposed at scratches and fractures in the coating. This behavior is quite unlike that of nickel, chromium, tin, copper, and lead, which as coatings ordinarily tend to accelerate corrosion of the iron base where exposed. The significance of this advantage for zinc is plain when it is considered that coated metal is probably never entirely free from pores and scratches that expose the base metal. Areas of exposed iron as much as $\frac{1}{4}$ in. across may be entirely protected by the surrounding zinc coating, in atmospheric exposure.

In addition to the galvanic protection described, zinc corrosion products tend to accumulate on the surface of the exposed iron, and some protective effect doubtless exists from these.

In the use of zinc-coated iron where the exposure is rather severe—in certain atmospheres and underground—it is frequently found advisable to apply paint on the zinc as an additional measure against corrosion. Since paint does not adhere to fresh hot-dip, zinc-coated surfaces, a roughening treatment before painting is necessary, either in the form of several months exposure to the atmosphere or etching with hydrochloric acid in toluol and alcohol (which remove grease). Copper or antimony salt solutions may also be used. The choice of the priming paint is important. The naturally

porous surface of a sherardized coat takes paint successfully without pretreatment. Electrogalvanized coatings are also successfully painted without pretreatment in some cases.

IMPURITIES IN ZINC

Sheet and strip zinc vary in impurity content from about .10% to .60% impurities—mainly lead, cadmium and iron. The slab zinc (spelter) used in hot-dip galvanizing varies from .01% to 1.5% in impurities. The purer grades are used in high-grade wire and sheet products where bending properties are important. For the spray-gun zinc wire and strip of widely varying purity are employed. Electrodeposited layers of zinc are the purest of any of the coatings. A highly refined zinc with less than .0001% impurities is a fairly recent development of scientific interest.¹².

The relation of impurities in zinc to corrosion behavior has certain features that should be mentioned. It has in the past been generally believed that the purer a metal is the more resistant it will be. This belief is based on the evidence that metallic impurities in a metal tend to set up minute galvanic couples with the metal itself to produce an accelerated corrosion of one or the other. The tendency for this to take place with zinc is strong in exposure to acids. Thus very pure grades of zinc dissolve more slowly in acids. It is reported * that iron in excess of .01 to .015%, depending somewhat on the other impurities present in the zinc, is likely to give rise to uneven corrosion or pitting in a dry cell. Copper in excess of .005% is not ordinarily tolerated for battery zinc. On the other hand lead and cadmium in proper amounts favorably affect battery corrosion.

Where the resistance of zinc is due to the accumulation of protective corrosion product, as in atmospheric exposure, impurities are usually an unimportant factor. On the other hand, the resistance of rolled zinc to outdoor corrosion is favorably affected to a slight degree by lead and cadmium. It is reported also * that the effect of copper, in certain compositions of zinc at least, is slightly beneficial.

An interesting sidelight on the effect of impurities on corrosion is the observation¹² that very high purity zinc (less than .0001% impurity), in the form of crystals as deposited in the condenser of the refining apparatus, had a much better resistance than high-grade commercial zinc in exposure to the atmosphere and to non-oxidizing acid solutions. This unusual resistance did not persist when the crystal form was remelted and cast or was rolled. It was found further that this "spectroscopically pure" zinc (rolled or cast), unlike electrolytic zinc, failed to evolve detectible hydrogen from a very dilute potassium chloride solution. In spite of this evidence of a positive effect of impurities, however, it was *generally* true that variations

* A. M. Pierce, private comment.

in the type and quantities of impurities as they exist in sheet zinc and zinc coatings carry no virtual demonstrated significance from the corrosion angle.

Proper control of impurities, particularly lead and tin, in die-casting alloys of high zinc content containing over .5% aluminum has been found to cure intercrystalline corrosion which resulted in swelling and cracking in tropical and subtropical atmospheric exposure.⁵¹

NATURE OF ZINC COATINGS

The structure of zinc coatings differs with the method of application. Under the influence of the heat involved in the hot-dip and sherardizing processes, alloys of iron and zinc form intermediate between the iron base and the outer zinc layer. These alloys are anodic to iron. Sprayed and electrodeposited zinc, on the other hand, consist of essentially pure metallic zinc. There is little to choose in specific corrosion resistance, though the greater thicknesses usually applied by the hot-dip method give this an advantage over the electro and sherardizing methods.

The thickness of galvanized coatings is usually expressed in ounces per square foot of surface or of sheet.* Hot galvanized coatings run from 0.00043 in. to 0.0021 in. Anything above 0.0013 in. is usually obtainable only on specification. Flux spots on hot galvanized sheets are cause for rejection.

Electrogalvanized coatings heavier than 0.0005 in. are usually obtainable only in special premium brands. Sherardized coatings are likewise thinner than hot-galvanized.

Zinc-coatings, though more abrasion resistant than tin-coatings, tend to wear away under scratching and rubbing. Here again the galvanic relation of zinc and iron is fortunate. The very satisfactory service of the common galvanized pail, in the face of the abrasion encountered in ordinary use, illustrates the good protection afforded by zinc coatings.

It has been commonly believed that where the metal must be bent, thin coatings are better than thick from the corrosion resistance standpoint. As an actual fact, however, there are indications that the reverse is true, even though the visible cracking at bends is more pronounced with the thicker coats. Evans²⁰ made tests in which different varieties of galvanized iron were bent sharply and immersed in a dilute sodium chloride solution. Each of six thinly coated specimens developed rust within 14 days, yet eight thickly coated specimens were unruined in this time, although they had suffered more conspicuous bend-cracking.

* 1 oz. per sq. ft. of surface = 0.00172 in.; 0.001 in. = 0.583 oz. per sq. ft. of surface.

TESTING THE NATURE OF COATINGS

Various methods of testing³¹ the thickness and efficiency of zinc coatings have been devised. The ferroxyl indicator test gives a fair idea of the continuity of the coating, and the so-called stripping tests, in which various acids are used in dissolving off the coating, are used for determining the thickness. In spray tests coatings are compared by the length of time it takes for rust to appear; the value of such tests lies more in affording comparisons between different samples—even then imperfectly—than in predicting the actual service life to be obtained.

GALVANIC CORROSION

Zinc stands between aluminum and iron in two-metal galvanic behavior, and in exposure to aqueous solutions it is characteristically anodic to iron, nickel, lead, tin, copper, and the various alloys of these metals. Aluminum and zinc couples lead to very little if any acceleration, with zinc tending to be the anode under most conditions.^{17, 53} Corrosion products on both zinc and aluminum suppress galvanic action. This perhaps would not be true in sea water or sea air exposure, where the presence of chlorides tends to break down protective films on aluminum.

Evans¹⁸ has demonstrated the galvanic protection of steel by zinc and has pointed out particularly how this effect differs quantitatively with solutions of different salts. The amount of zinc sacrificed is greater sometimes than the amount of steel saved. The specimens, of equal area, were partially immersed for 39 days. (See Table 52.)

TABLE 52.—Zinc : Steel Couples vs. Various Solutions.

	Corrosion Rate — Mg. per sq. dm. per day			
	Uncoupled		Coupled	
	Zinc	Steel	Zinc	Steel
M/20 Magnesium sulfate...	+	13	17	+
M/20 Sodium sulfate.....	56	50	165	+
M/20 Sodium chloride.....	50	50	150	+
M/200 Sodium chloride....	22	35	43	+
Carbonic acid.....	2	14.7	7.5	+
Calcium bicarbonate	+	4.5	+	+
Tap water (hard)	+	14	+	+

A use for zinc of interest from the standpoint of corrosion and based on its electrolytic behavior is as a sacrificial anode in couple with iron and brass, the purpose being to protect equipment constructed of these metals at the expense of readily replaceable slabs of the zinc. Use of this principle is made in the oil-fields where zinc is placed in couple with the iron tubing and casing of an oil-well assembly. The method has been employed also in the protection of underwater iron parts of small ships, and in sea

water condensers. The main short-comings of this sacrificial corrosion lie in the fact that the distance over which the influence of the anodic zinc is felt is often measured in inches, rather than in feet as so often imagined, and that the amount of zinc sacrificed may be greater than the steel saved. As corrosion products develop on zinc its powers of protecting iron are diminished in both weak and strong electrolytes, i.e. tap-water and sodium chloride solution. Zinc protective plates are still considerably used.

A second commercially important use of zinc involving its galvanic behavior is as the anode pole in the common dry cell. In closed circuit in a mixture of ammonium chloride and manganese dioxide, with carbon as the cathode, the zinc passes into solution and so produces the current. The reaction is not reversible.

Zinc plates have been used likewise as a protection to iron in marine boilers. A recent paper⁴ points out, however, that the protection so afforded, though real enough, is not electrolytic but rather is due to the using up of the oxygen in the water by the normal uncoupled corrosion of the zinc. The oxygen thus becomes unavailable for iron corrosion.

DEFINING NON-CORROSIVE NEUTRAL RANGE OF AQUEOUS SOLUTION

Zinc has useful resistance only in a relatively narrow, neutral range of solution, this resistance being due in the simplest case to a protective film of hydrate, abetted in the case of impure solutions by other precipitated corrosion products and compounds deposited from solution. The hydrate is soluble on both the acid and alkaline sides of this neutral zone.

Work by Roetheli, Cox and Littreal⁴⁸ has very effectively drawn the limits of the neutral, hydrate-forming zone in tests in distilled water with hydrochloric used to throw the solution acid and sodium hydroxide alkaline. The solutions were kept rather strongly agitated. Figure 16 shows the results.

The hydrate is seen to have been most protective between the neutral point, pH 7, and pH 12.5. The fact is brought out that the exact shape and location of this curve is typical probably only of the particular set of conditions under which these tests were made. Factors such as agitation, aeration, salts in the solution, and temperature, in conjunction with hydrogen-ion concentration, affect the characteristics of film formation. These investigators conclude "in a universal sense the condition of low or negligible corrosion probably lies between pH values of 6 and 8 as minima and 11 as a maximum."

Cox¹¹ has on another occasion established the effect of temperature on behavior in distilled water. The specimens were constantly in motion in the solution, and the solution aerated with a stream of unwashed air

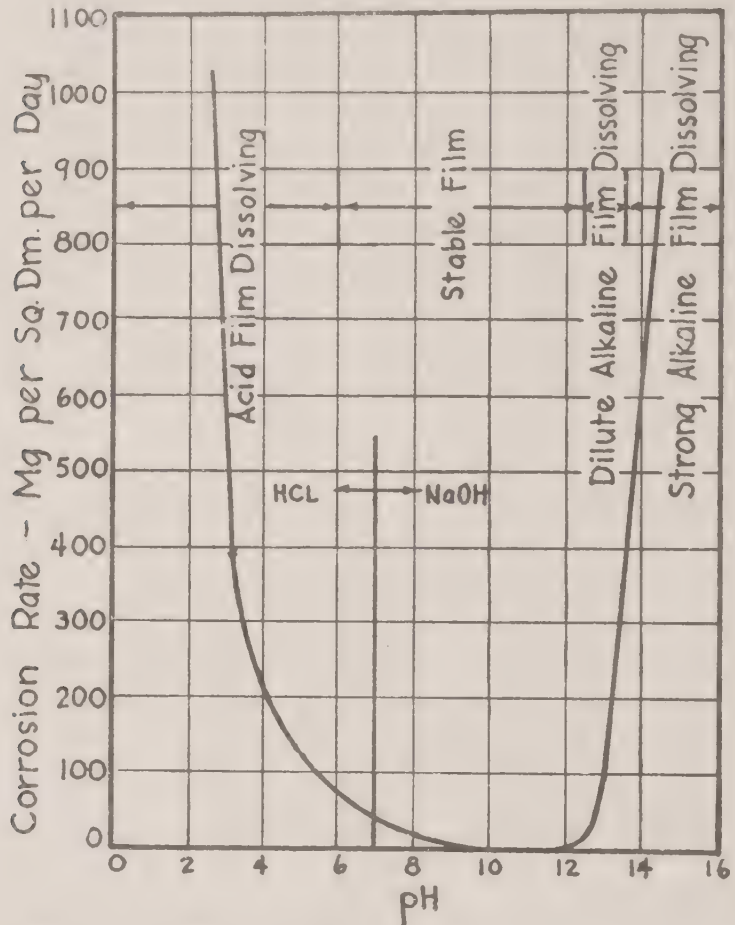


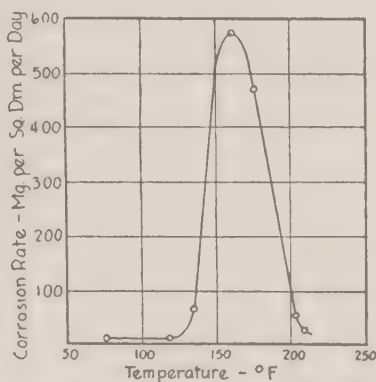
FIGURE 16. Effect of pH Value on Corrosion of Zinc.

TABLE 53.—Zinc vs. Distilled Water.

Temp. ° F.	Appearance of Precipitate	Tenacity of Precipitate
68	Definitely gelatinous	Very adherent
122	Slightly less gelatinous	Adherent
131	Mostly granular	Non-adherent
149	Decidedly granular, becoming flaky, compact	Non-adherent
167	Decidedly granular, flaky, compact	Non-adherent
203	Compact, dense and flaky	Adherent, removed by bending specimen and fracturing scale
212	Varies from grayish white to black, very dense; resembling enamel	Very adherent and difficult to remove by mechanical means

bubbles. The duration of test was 15 days. The results are given in Figure 17. Examination of the zinc hydrate film showed that the strong increase in corrosion coincided with a change in the nature of the film from an adherent gelatinous state to a non-adherent granular state. (See Table 53.)

FIGURE 17. Zinc vs. Distilled Water; Effect of Temperature.



These results on change of film structure with temperature, and those preceding on the limits of the neutral relatively non-corrosive range of solution, are very valuable as background to an understanding of the corrosion resistance of zinc. A rate of 10 mg. per sq. dm. per day is sufficiently low to indicate moderately good resistance, whereas rates of .5 to 2 mg. per sq. dm. per day are typical of the low degree of action of atmospheres on zinc.

Behavior under acid, alkaline, and neutral conditions will now be discussed in order.

ACID CONDITIONS

Acids corrode zinc with strong evolution of hydrogen. As already noted in Figure 16 only very dilute concentrations of acid are required to push corrosion rates beyond the limits of usefulness. Thus hydrochloric with a pH of 4 yielded a rate of 200 mg. per sq. dm. per day.

A good illustration of behavior, under different exposure conditions, against a strong acid and a weak acid—hydrochloric and acetic respectively—is given by the data in Table 54.³⁰ The duration was 48 hours following previous 48-hours exposure, and the tests were made at room temperature. One normal hydrochloric has a pH value of about 1, one normal acetic a pH of about 3.

A zinc coating of .002 inch thickness on steel would be entirely dissolved, at a rate of 280 mg. per sq. dm. per day, in 13 days time.

TABLE 54.—Zinc vs. Acid Solutions.

	Corrosion Rate—Mg. per sq. dm. per day	
	Hydrochloric — 1 N	Acetic — 1 N
Total immersion		
Quiet	7,500	3,250
Air-agitated	6,500	3,700
Alternate immersion		
Continuous	23,000	4,500
Intermittent	22,500	850
Spray (30 days)	280	470

A use for zinc that depends on corrodibility rather than resistance is in photo-engraving, particularly for newspaper work. This use is based on the behavior of certain organic acids, notably oleic and arabic, in yielding corrosion products on zinc plate that attract or repel ink.

ALKALINE SOLUTIONS

Zinc like aluminum is amphoteric, and as a result is susceptible to the attack of alkaline solutions in much the same manner, although not so actively so, as aluminum. The results of Figure 1 indicate that the zinc hydrate film that is protective in the neutral zone becomes soluble as the pH moves above 12. The chemistry involved is reaction between zinc hydrate and alkali to form readily soluble zincate. The presence of oxygen promotes this reaction, although, in the higher hydroxide concentrations at least, oxygen is not necessary for rapid reaction rates.

Aqueous ammonia corrodes zinc rather readily with the formation of a complex soluble hydrate of zinc and ammonia.

Some idea of the effect of alkaline solutions is given by the data in Table 55.³⁰ The duration was 48 hours following previous 48-hours exposure, at room temperature.

TABLE 55.—Zinc vs. Alkaline Solutions.

	Corrosion Rate—Mg. per sq. dm. per day	
	Sodium Hydroxide—1 N	Ammonium Hydroxide—1 N
Total immersion		
Quiet	90	60
Air-agitated	170	140
Alternate immersion		
Continuous	1850	550
Intermittent	450	60
Spray (30 days)	3	<1

These moderately strong alkaline solutions are much less actively corrosive than corresponding concentrations of acids, yet with the exception of the spray exposure may be considered too corrosive for zinc to be useful with them.

NEUTRAL SOLUTIONS

Of the neutral solutions distilled water is relatively high in its action on zinc. An idea of rates may be gained by the following data, from 24 hour tests at room temperature on cast 99.97% zinc⁸:

	<i>Mg. per sq. dm. per day</i>
Distilled water	
Quiet suspension	53; 76
Air-agitated	167; 199
Agitated with carbon dioxide	143
Agitated with air	33

Thus perhaps a fair average range of rates in distilled water would be 30 to 200 mg. per sq. dm. per day. The specimens were pitted in these tests, so that actual penetration rates would tend to be higher.

It seems generally to be the impression that distilled water is more corrosive to zinc than waters carrying salts.² In one set of tests⁷ metallic zinc was corroded from 4 to 6 times as rapidly by stagnant distilled water as by sea water or by 2.5% sodium chloride.

A good example of corrosion rates for zinc submerged in a number of different salts of various concentrations is given in Table 56.²⁹ The solutions were for the most part quiet, and exposed at the surface to air. The specimens were submerged 2.3 in. below the surface.

TABLE 56.—Zinc vs. Salt Solutions.

Salt	Conc. grams per liter	Temp. ° F.	Duration Days	Corrosion Rate Mg. per sq. dm. per day
None		54	64	10
Sodium chloride	5-400	54	64	18-2.6
Potassium chloride ..	5-300	54	65	18-0.9
Potassium nitrate	5-100	46	189	3-1.1
Sodium sulfate	5-300	54	60	12-1.8
Potassium sulfate ..	5-100	54	57	11-0.5

These rates are low because of the quiet submersion condition. Evans²³ obtained a rate of approximately 110 mg. per sq. dm. per day each for $\frac{3}{4}\%$ solution of potassium chloride and $1\frac{3}{4}\%$ potassium sulfate, on electrolytic zinc specimens partially immersed in the quiet solutions.

A good illustration of the action of a typical, moderately corrosive salt, sodium chloride, and a relatively non-corrosive, special film-forming salt, potassium dichromate, is given by the data in Table 57.³⁰ The tests were made at room temperature, for a 48-hour period following 48-hours previous exposure.

TABLE 57.—Zinc vs. Salt Solution.

	Corrosion Rate—Mg. per sq. dm. per day	
	Sodium Chloride—1 N	Potassium Dichromate—1 N
Total immersion		
Quiet	23	.7
Air-agitated	65	.7
Alternate immersion		
Continuous	600	1.5
Intermittent	700	1.5
Spray (30 days)	11.5	<.1

Aeration-agitation for salts like sodium chloride is accelerating, and alternate immersion is seen to be extremely accelerating. Spray exposure on the other hand is a relatively mild condition. A still further set of data⁸⁸ covers the effect of several alkaline salts on zinc under quiet partial immersion conditions. (See Table 58.)

TABLE 58.—Zinc vs. Salt Solutions.

Condition	Mg. per sq. dm. per day
5 hrs., 150° F.	
Sodium carbonate—.5%	38
Sodium phosphate—.5%	24
5 days, 70° F.	
Sodium hypochlorite .	
.236 grams per liter available	
chlorine	21

Submerged in 10% ammonium chloride solution for 30 days the rate of attack on zinc was found to be 20 to 70 mg. per sq. dm. per day.¹⁶

The rates in the foregoing paragraphs afford a fair picture of the order of resistance of zinc to neutral aqueous solutions.

The effect of temperature on corrosion of zinc has already been mentioned in connection with Figure 17. Confirmation of the fact that increasing temperatures cause much greater corrosion is found in the following results of Baylis⁶ on the quantity of hydrogen evolved from zinc submerged in tap water. (See Table 59.)

TABLE 59.—Zinc vs. Tap Water.

Temperature °F.	Hydrogen gas in c.c. per 24 hrs. at 68° F.
68	1.3
98	2.2
127	3.6
203	120
212	175

Baylis⁶ also found that the rate of hydrogen evolution dropped off very appreciably with time.

Speller⁵² has given corrosion rates, for cast zinc exposed 6 months in tap water at 158° F., of 16 to 33 mg. per sq. dm. per day for unaerated water, and 28 to 51 mg. per sq. dm. per day for aerated.

Sheet zinc in submerged aqueous corrosion is characteristically pitted. This is not observed with galvanized iron, the reason being that the progress of localized corrosion is prevented by the underlying iron, the latter remaining substantially unattacked so long as the zinc coating is not completely removed from the vicinity of the bared iron.

Evans¹⁹ has made an extremely interesting study of the inception and progress of attack of zinc partially immersed in aqueous solutions. Specimens held at an angle of 15° from the vertical in distilled water corroded with the development of vertical tracks bounded by two white lines, "suggesting that some heavy liquid was being exuded from these points and was descending in streams, depositing an insoluble body on either side."

Specimens immersed in potassium sulfate, sodium chloride, and magnesium sulfate corroded in a horizontal zone at the bottom of the specimen with an uncorroded zone between this and the water level. The boundary between these zones climbed up with time to approach the top. The specimens in addition corroded visibly at points, as in the case of distilled water, at lines or scratches and at points along the edges. The spots at which corrosion started were very fine cavities originally present in the metal surface, finger marks, rolling defects in the surface.

These observations indicate clearly the extreme susceptibility of zinc to localized attack and to the establishment of concentration cells.

An interesting long-time test in sea water has been made by Friend.²⁷ A zinc bar was included with other metals in 4-years exposure to Bristol (England) Channel water at such a location that the bars were submerged 93% of the time. The average over-all corrosion rate for zinc was 18 mg. per sq. dm. per day, though the surface was roughly pitted to depths of about .035 inch (corresponding to 45 mg. per sq. dm. per day maximum rate). The order of attack, both general and localized, was similar to that of iron and steel.

On the other hand—and a very important point—a galvanized iron bar suffered no appreciable localized attack, with traces of zinc remaining on the bar at the end of the test.

The protective corrosion product that develops on zinc in sea water has been found⁹ to consist mainly of carbonate, hydroxide, and oxychloride.

The susceptibility of zinc to localized attack in submerged exposure of waters and salts is sufficient to prevent the successful use of solid zinc under these conditions. On the other hand the freedom from localized attack characteristic of zinc coatings on iron and steel, combined with the strongly protective effect of even damaged and corroded coatings, gives

the coating a far greater usefulness than the behavior of zinc itself would suggest.

The use of zinc-coated iron and steel pipe for carrying water is very common, zinc being applied both inside and out. Ordinarily the zinc deposits are heavy, usually about 50% as heavy on the inside as on the outside. In the case of buried pipe, acid and alkaline soils are more rapid in their attack than the neutral range of soils. Often protection is given the outer zinc surface by paint.

There is a variation in corrosion rates among different types of waters according to the salts and gases carried in the water. In general, soft waters are more corrosive to zinc than waters carrying calcium salts. Chloride fresh waters are stated to be more corrosive than those without appreciable chloride. Certainly elevated temperatures and strong aeration and agitation are accelerating conditions.

Just what corrosion rate ranges for zinc coatings are to be expected in fresh waters is rather a question. Speller,⁵² as already stated, gives rates of 15 to 50 mg. per sq. dm. per day in water at 158° F. over a six-months period. The rates in dilute salt solutions in quiet exposure at ordinary temperature, given already,²⁹ run around 3 to 15 mg. per sq. dm. per day. This would seem a fair typical range for quiet waters at ordinary temperatures, with aeration an accelerating condition, and deposition of calcium carbonate and certain other compounds suppressing.

Galvanized iron is commonly used in equipment handling refrigerating brines.^{52, 57} To reduce the attack of unprotected iron the brine is often made alkaline, yet if made alkaline to the extent that the corrosion of iron is suppressed the brine becomes corrosive to the zinc. A pH value of 9.5 to 10 seems the best compromise. An interesting comparison of attack of zinc and iron is given by the data in Table 60. The specimens were exposed in air-agitated brines.⁵⁷

TABLE 60.—Zinc vs. Brines.

Conc. pH	Relative Corrosion Rates			
	Calcium Brine		Sodium Brine	
	Iron	Zinc	Iron	Zinc
4	100	235	100	115
7	100	165	100	55
10	100	120	100	3
12.6	100	90*	100	100*

* Pitted.

FOOD PRODUCTS

Neither sheet zinc nor galvanized iron and steel are used to a great extent for handling food products, (except where exposure is largely

atmospheric), both because so many foodstuffs are sufficiently acid to attack zinc rather strongly, and because other available metals, notably tin, are considered less toxic than zinc, or even non-toxic. The advantage in cost that zinc-coated metal has is therefore of little avail in this field. The wide use, on the other hand, of galvanized pipe and tanks for handling household water supplies has already been mentioned.

Some idea of the solubility of zinc in acid foodstuffs is given by the values in Table 61 for zinc absorption in parts per million of solution after being held in galvanized iron pails.⁴⁹

TABLE 61.—*Zinc vs. Milk, Fruit Juice and Waters.*

	Zinc—p.p.m.		pH Value			Acidity, in c.c. of 0.1 N acid per liter	
	17 hrs.	41 hrs.	Start	17 hrs.	41 hrs.	17 hrs.	41 hrs.
Tap water	5	21	7.2	8.4	8.8	0	0
Distilled water.	9	27	6.2	7.5	8.2	1	0
Carbonated water	193	181	5.2	6.4	6.9	348	96
Milk	438	1054					1109
Orangeade	530	854	3.7			397	533
Lemonade	1411	2700	2.6			493	366

Milk corrodes zinc at rates of 20 to 80 mg. per sq. dm. per day under aeration-agitation conditions, 86° to 203° F.³⁸ In other tests,³⁷ in quiet partial immersion in various milk products, rates of 1 to 60 mg. per sq. dm. per day were obtained.

TOXICITY OF ZINC

The likelihood of waters being toxic^{13, 24, 47, 50, 54} when containing zinc absorbed from ordinary exposure to the galvanizing on pipes is extremely slight. Howard³⁴ has observed that waters conducted through galvanized pipe commonly carry up to 5 parts per million zinc and rather frequently carry 10 to 15 parts per million. Clark¹⁰ has reported zinc ranging from 0 to 3 parts per million in water drawn through typical galvanized service pipes, less than 100 feet in length, in ordinary use, and somewhat higher contents in water that has stood over night. These zinc contents seem negligible, from the toxicity point of view, when it is considered that common foodstuffs as found in nature may carry many times these.

Zinc is believed to be non-cumulative in its physiological effect.⁵⁴

After reviewing the available information on toxicity, Anderson, Reinhard and Hammel,¹ have stated as follows:

"In the absence of complete information it is difficult for a layman to arrive at a true estimation of the importance of the zinc content of water. Even at 40 milligrams per liter it is doubtful that much more than 100

milligrams will be ingested daily, since few people will use much more than 2½ liters (3 quarts) of water daily for drinking and in cooked food. Most foodstuffs contain zinc. The following menu¹⁴ of a test meal contains from 225 to 275 milligrams of zinc: three-fourth yeast cake with anchovies, chopped olives and mayonnaise, twelve oysters (raw), oyster soup (eight oysters), duck-bread stuffing, applesauce, corn on the cob, wheat bran pudding, bread and butter, strawberry gelatin-whipped cream, coffee and sugar. No ill effects were noted from this meal.

"The normal rate of loss of zinc from the human system amounts to about 3 to 20 milligrams per 24 hours with an average of about 10 milligrams.¹⁴ These amounts represent those taken in normal food. There is every indication that were larger amounts taken in daily the loss would become correspondingly large and no ill effects would result. In the Drinker, Thompson and Marsh¹⁵ experiments continued feeding of amounts of zinc far beyond what normal diet would involve, produced no ill effect on rats, cats and dogs.

"On the basis of all of these considerations the writers feel safe in considering waters containing up to 40 milligrams per liter safe for human consumption."

ATMOSPHERES

The behavior of zinc in atmospheric exposure has been summarized by Hubbell and Finkeldey³⁵ as follows:

"Like several other metals which exhibit marked resistance to corrosion, in the atmosphere, bright zinc rapidly tarnishes when first exposed, forming a smooth tightly adherent protective film. This film is apparently a combination of zinc oxide, zinc carbonate and zinc hydroxide. It is not readily soluble in ordinary atmospheric waters nor easily destroyed by other atmospheric agencies.

"The film varies in thickness depending upon the exposure conditions, probably reaching a maximum thickness of .0003 in. If removed or worn thin by abrasion, it is renewed in a few days to its original thickness. Some idea of the insolubility of this film in ordinary atmospheres may be gained from the fact that there are in Europe zinc roofs over one hundred years old and still giving service. However, the film is more readily attacked in atmospheres high in SO₂ and CO₂, which accounts for the more rapid destruction of zinc-coated products in the Pittsburgh district."

These authors have also generalized as follows in respect to the use of galvanized metal in atmospheric exposure:

"1. For all outdoor and severe indoor service use only materials heavily galvanized by the hot-dip process. Sheet and wire products should be purchased under specification to secure heavy enough coatings to give long life. All articles whose manufacture requires severe deformation should be galvanized after fabrication.

2. For semi-protected outdoor and equivalent indoor exposures, sherardized or light weight hot-dipped coatings are satisfactory. Sherardizing is especially adapted to small castings, fittings, bolts and nuts.

3. For indoor exposures under normal conditions electrogalvanized coatings will be satisfactory. The process is used chiefly to coat small working parts of machines and similar apparatus requiring protection from rusting for their proper mechanical performance."

Basing their opinion on collected data, Hubbell and Finkeldey further have given an idea of the life in years to be expected of sheet zinc and zinc coatings in exposure to different types of atmospheres. (See Table 62.)

TABLE 62.—Zinc vs. Atmospheres.

	Expected Life in Years			
	Rural	Sea Coast	Semi-Industrial	Heavy Industrial*
Commercial rolled zinc .020"	50-75	50	20-30	10-15
Galvanized sheet				
1.25 oz. per sq. ft. of surface	30-35	20-25	15-20	8-10
1.00 oz. per sq. ft. of surface	20-25	15	10-15	6- 8
.6 oz. per sq. ft. of surface	8-10	5- 8	5	3- 5
.2-.3 oz. per sq. ft. of surface	3- 4	2- 3	1- 2	1

* Compare with Figure 18.

The rate of attack on zinc, according to tests by Vernon ⁵⁵ in indoor atmospheres, is constant after about one-day exposure, perhaps often less than one day. The initial rate is faster than this constant but the corrosion product film that first develops when freshly abraded zinc is exposed is protective. A visible corrosion product accumulates, granular in nature; it is some continuous film beneath this granular product that affords the protection, however.

The rate of atmospheric attack on zinc is therefore slow. In an investigation of the fundamentals of this attack, Vernon ⁵⁶ determined the rate in outdoor London exposure, with specimens unprotected from the wash of rain, to be less than 1 mg. per sq. dm. per day. In one series of 100-weeks duration, the metal washed off with the rain water and the metal content of the *in situ* corrosion product was determined, to give the following values:

Zinc removed by rain-water	1.154 gms.
Zinc corroded and <i>in situ</i>	0.058 gms.
Total corroded zinc	1.212 gms.
Corrosion rate	0.78 mg. per sq. dm. per day

In a second series of tests at the same location, of 225-weeks duration, a corresponding rate of 0.97 mg. per sq. dm. per day was established. The latter rate represents the actual average weight loss of the specimens multiplied by a factor whose value was based on the experience of the first series of tests, to take into account the metal carried in the *in situ* corrosion product.

The *in situ* corrosion product in both series consisted largely of oxide, hydroxide and combined water, but in part of sulfide, sulfate, and carbonate.

Hudson ³⁶ obtained the rates in Table 63 for zinc in a year's exposure, outdoors and unprotected from rain, in various atmospheres.

Long-time tests by Patterson,^{40, 41, 42} Vernon,⁵⁸ and Prost ⁴⁵ confirmed the similarity between different grades of zinc, at least insofar as weight change is an indication.

TABLE 63.—Zinc vs. Atmospheres.

	Mg. per sq. dm. per day	
	Electrolytic Zinc	Ordinary Zinc
Rural585	.575
Suburban985	.94
Mild industrial	1.32	1.29
Urban	1.88	1.94
Marine99	1.04

The weight-loss rates for specimens of sherardized and hot-dip galvanized sheet, and of rolled zinc, in New York City atmosphere, were found to be 0.7 mg. per sq. dm. per day, with no important difference between the types.³³ The test period was one year.

In a study²⁵ of galvanized sheet carrying different thicknesses of zinc coatings, in exposure over a 6 to 7 year period at Pittsburgh and Altoona, Pa., respectively, the results of Figures 18 and 19 were obtained.

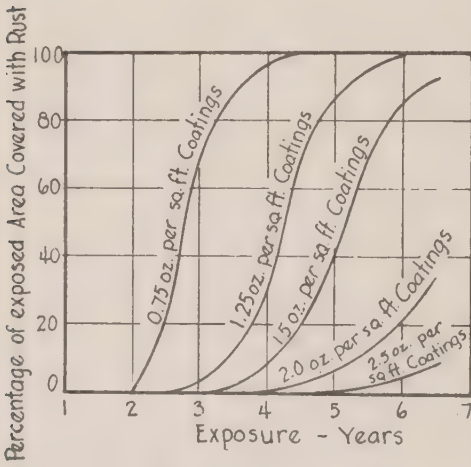


FIGURE 18. Galvanized Iron vs. Atmosphere at Pittsburgh, Pa.

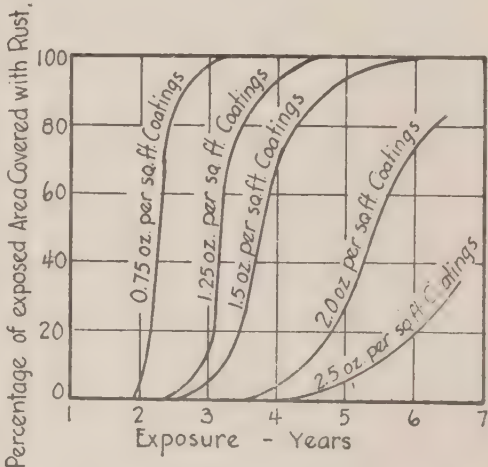


FIGURE 19. Galvanized Iron vs. Atmosphere at Altoona, Pa.

Assuming the 0.75 oz. per. sq. ft. sheet (1225 mg. of zinc per sq. dm. of surface) to have a zinc layer of even thickness, the maximum corrosion rate in these tests corresponding to a two-year period for the first appearance of rust would be about 1.7 mg. per sq. dm. per day. Likewise the rate corresponding to a 4½-year period for total disappearance of zinc would be (Pittsburgh) 0.75 mg. per sq. dm. per day. The rate corresponding to the period to produce rust over 50% of the surface on the Pittsburgh sample would calculate to 1.2 mg. per sq. dm. per day.

An interesting result, in that the exposure period was 7 years, is that of Friend.²⁸ The zinc bar was exposed on a roof in Birmingham (Eng.). The rate was 1.15 mg. per sq. dm. per day, "with small pinhole pitting."

The effect of impurities in zinc on its resistance to atmospheric corrosion is almost negligible, according to the results of Patterson's tests.⁴⁰ He found both in moist indoor and in outdoor atmosphere a greater attack during the winter months due possibly to the more acid nature of moisture, and found that excessive humidity led to stronger corrosion. Over a 14 months period in outdoor London exposure zinc was corroded at a rate of just under 1 mg. per sq. dm. per day.⁴²

An interesting set of observations on the appearance of high grade commercial zinc specimens after exposure for a year at various locations is quoted below ²⁵:

Pittsburgh, Pa.	Light gray thin uniform adherent film
Altoona, Pa.	Light gray thin uniform adherent film
State College, Pa.	Light gray uniform adherent film
New York City	Light gray thin uniform adherent film
Sandy Hook, N. J.	Light gray uniform adherent film
Rochester, N. Y.	Light gray thin uniform adherent film
Key West, Fla.	Light gray uniform adherent film
Phoenix, Ariz.	Distinctly tarnished with areas of light gray adherent film
La Jolla, Calif.	Heavy white bulky scale of irregular thickness

At La Jolla, high humidity and salt spray conditions prevailed.

A very important feature of the atmospheric resistance of zinc is the fact that for the corrosion product to become protective in the highest degree a combination of alternating wet and dry exposure is best. Evans ²² has called attention to this and cites a case where galvanized iron exposed to the atmosphere of the Scilly Islands was in excellent condition after 15 years, whereas new galvanized iron exposed at the same location began to rust within a year. The exposure conditions in respect to alternate damping and drying were possibly more favorable in the first instance to the initial development of good protection, but it is much more likely that the relative thickness of the zinc coatings was responsible for the difference.

Cases of abnormal corrosion of zinc flashings and gutters are said to have been traced to the action of organic acids leached from shingles of redwood, oak, and cedar, or from built-up or tar roofs, or to the action of rain-water shed from copper roofs and flashings. The evidence is very doubtful however. On the other hand corrosion is known to be accelerated by accumulations of coal ash high in iron, nails and other tramp iron. Often, too, zinc-coated sheets carry a white bloom after storage, particularly in humid and seacoast atmospheres. This latter does not signify pronounced corrosion at all, in fact it would be very unusual for pronounced corrosion to occur in this way.

The beneficial effect of zinc coatings on steel is shown by the results of fatigue tests in carbonate water exposure.³² The tests were made in a

rotating beam type fatigue machine, run at a speed of 1750 r.p.m. for 10^7 cycles (4 days). In Table 64 are the results.

TABLE 64.—*Galvanized Steel vs. Carbonate Water.*

	Fatigue Value at 10^7 Cycles Lbs. per sq. in.
Uncoated steel, in air	60,500
Uncoated steel, in water	20,000
Electroplated steel, water	60,500
Sherardized steel, water	43,500
Galvanized steel, water	43,500

The poorer behavior of sherardized and galvanized specimens was believed due to a notch effect related to the zinc-iron alloy layers between the zinc coating and the steel. In other words this presumably was not due to poorer inherent protection against corrosion.

HIGH-TEMPERATURE DETERIORATION

Zinc has little utility at temperatures above the boiling point of water, since the strength of zinc is deficient in this range and the behavior of zinc coatings against superheated steam and oxidizing and sulfidizing gases is generally poor. The melting point of zinc is 786° F. Pilling and Bedworth⁴³ determined that dry oxygen at slightly below this— 752° F.—slowly oxidized zinc, forming a milk-white coating of oxide that was partially protective.

ZINC

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Chapter VIII

Cadmium Plate

In the field of corrosion resistance cadmium plays a limited role. Its use is based on the protection it gives as an electroplated coating on iron and steel.¹⁵ In its general effectiveness cadmium is rather like zinc.* In cost cadmium plate is at a definite disadvantage compared with zinc plate.

Like zinc, cadmium behaves anodically to iron in atmospheric and neutral aqueous exposure. With these metals, therefore, iron where exposed at pores and breaks in the coating is prevented from corroding. This behavior contrasts with lack of protection and the definitely accelerating effect chromium and nickel exert on corrosion of bare iron. The anodic relation is necessary for reasonably successful behavior in outdoor atmospheric and submerged exposure since metallic coatings are characteristically porous. Whereas rust will "bleed" from pores in chromium or nickel plate, rusting is largely prevented or is at least only superficial when steel is exposed at small areas in the case of zinc and cadmium plate.

Four extremely useful reports have been made on long-time atmospheric exposure of cadmium-plated ferrous metal. The first is that of Hocker⁸ in which he offers a critical analysis of the extensive long-time outdoor exposure tests of the American Society for Testing Materials.¹¹ The behavior of cadmium-plated specimens is summarized in the curves in Figures 20, 21 and 22.

It is interesting to see that in the more corrosive industrial atmospheres a year's exposure has led to rusting of 60 to 90% of the specimen area, whereas in the rural (State College) atmosphere the rusted areas have ranged from 4 to 12% of the surface. In the marine atmospheres behavior was intermediate. The same relation among the atmospheres held for zinc-coated specimens as well, although the damage to zinc-coated metal was in every case less than that of cadmium.

Tests by Hippensteel and Borgmann⁷ in outdoor New York City exposure have supplied an idea of actual corrosion rates of cadmium plate. The plating was approximately .0008 in. in thickness. The corrosion rate over a year's duration was 2.5 mg. per sq. dm. per day (.0004 in. per year).

* See Gillett's discussion of relative merits.⁶

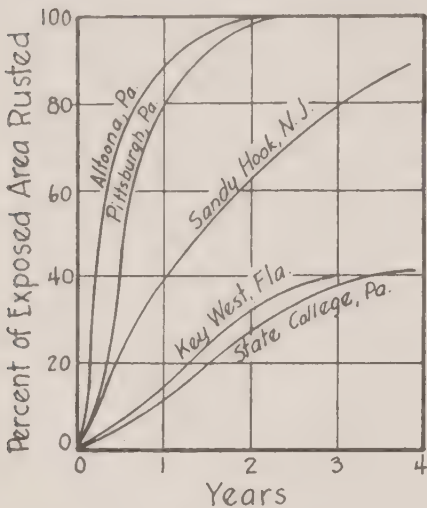


FIGURE 20. Cadmium Plate vs. Atmosphere. Plate thickness 0.14 to 0.24 oz. per sq. ft.

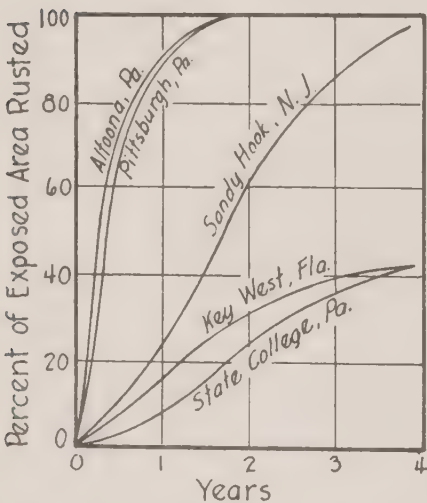


FIGURE 21. Cadmium Plate vs. Atmosphere. Plate thickness 0.27 to 0.37 oz. per sq. ft.

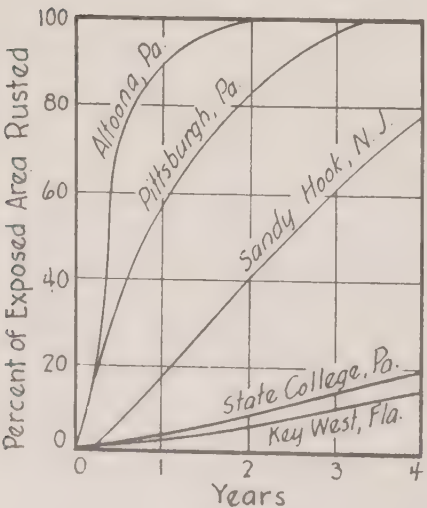


FIGURE 22. Cadmium Plate vs. Atmosphere. Plate thickness 0.43 to 0.67 oz. per sq. ft.

The third set of very useful tests is that of Patterson.¹² In open exposure in London atmosphere the corrosion rate for cadmium plate was 1.5 mg. per sq. dm. per day for 3-month's exposure and 4.1 mg. per sq. dm. per day for 9-month's exposure, using the same specimen. Over a 76-day period solid cadmium gave a rate of 3.5 and cadmium plate a rate of 4.2 mg. per sq. dm. per day. In indoor exposure, with an average humidity of 55%, the rate for cadmium plate over a 90-day period was 3, over 250 days was 1.2 mg. per sq. dm. per day.

Finally, in outdoor tests made under the auspices of the American Society for Testing Materials and the American Electroplaters' Society,¹ cadmium-plated steel specimens were exposed 18 months with results given in Table 65. The higher the "score" the better the behavior.

TABLE 65.—*Cadmium Plate vs. Atmosphere.*

	Score		
	.0002 In. Cadmium	.0005 In. Cadmium	.001 In. Cadmium
Industrial			
Pittsburgh	44	82	86
New York	37	64	77
Non-industrial			
Washington	97	100	98
State College	100	100	100
Marine			
Key West	85	85	85
Sandy Hook	86	93	91

The "score" relates to per cent of surface rusted as follows:

Score	Per Cent of Surface Rusted
100	0
80	0-5
60	5-10
40	10-20
20	20-50
0	50-100

The authors of the report felt that only the results in the industrial atmospheres were conclusive.

The four sets of data discussed above give a fair idea of behavior to be expected of cadmium plate in atmospheric exposure.

As already stated, cadmium is characteristically anodic to iron in atmospheric and aqueous exposure. That this relation is true in the atmosphere is recognizable from the appearance of cadmium plate following exposure. With respect to submerged exposure Rawdon¹⁴ has demonstrated the fact

by immersing an iron:cadmium couple in $\frac{1}{2}$ normal sodium chloride. In 48-hours exposure iron remained unruined at distances of almost an inch from the cadmium, which was the limit of the test set-up. The cadmium on the other hand was distinctly etched. The iron area was several times that of the cadmium. The sacrificial corrosion of cadmium has also been demonstrated in an English investigation.²

Corrosion rates in water and salt solutions are almost entirely lacking. Evans⁴ immersed cadmium in a 1 normal solution of potassium chloride for 70 hours. The solution, previous to the immersion of the specimen, was saturated with air. The corrosion rate was 22 mg. per sq. dm. per day, which was of the same order as that for zinc. In other tests¹⁰ the rates in quiet and aerated sea water were less than 2 mg. per sq. dm. per day, in 75-day tests, behavior being a good many times better than that of zinc. The latter fact is also indicated by observations of Dornauf³ on submerged exposure. These results would indicate that for submerged exposure in neutral aqueous conditions the resistance of cadmium-plated ferrous metal might be to some extent useful.

Cadmium plate is a decided protection to steel in corrosion fatigue exposure. Tests were run in a carbonate tap water⁶ on a steel with an air-fatigue limit of 60,500 lbs. per sq. in. The apparent fatigue limits (10^7 cycles, 1750 r.p.m.) in water were as follows:

<i>Fatigue Limit in Water.</i>	
	Lbs. per sq. in.
Bare steel	20,000
Cadmium-plated steel	46,000

The plate was .00022 in. in thickness.

The acid resistance of cadmium is of a low order. It is well known that cadmium has a high over-voltage value, and therefore in air-free acid solutions corrosion would be expected to be extremely slow. In the presence of oxygen or other oxidizer in solution, on the other hand, cadmium is of poor resistance. Cadmium plate is not a useful material in acid exposure.

With respect to alkaline solutions it is significant that cadmium, unlike zinc and aluminum, is not amphoteric and therefore does not suffer the intense attack characteristic of aluminum and zinc in moderate to strong caustic alkaline solutions.^{2, 9} Susceptibility of zinc to this type of attack has been a limitation to its use in handling brines made alkaline for the sake of minimizing corrosion of bare iron. Cadmium plate has an advantage in this field; an example is the use of cadmium plate in laundry equipment handling alkaline solutions.

Indications of behavior of cadmium coatings in exposure other than atmospheric are not extensive.^{2, 13}

CADMIUM

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Chapter IX

Tin and Tinplate

Corrosion resistance is the most important property accounting for the use of tin, both in the solid form and as a coating to other metals. Thus on this basis block tin pipe is used for handling beer, and solid tin is rolled into foil used for silvering mirrors and for wrapping confectionery, toilet soap, tobacco and other products. Sheet tin is used for collapsible tubes for dental creams and similar products.

Tinplate, or tin-coated steel, is characterized by good appearance, lightness, ductility, ease of soldering and seaming and especially for suitability for mass production processes. Tin plating is an old process; it was a thriving industry in Fifteenth Century Europe. The hot-dip plating process, originally used, is largely in vogue at the present time. Electrolytic deposition of tin is practiced to a considerable extent. A further method, used for plating small articles like pins and clasps, is the "contact" process, in which the iron to be plated lies in contact with plates of zinc in a solution of tin salts. The tin plates out on the iron.

Coatings of tin are used extensively on the heavy copper cooking kettles and containers used in ship galleys and hotel kitchens, and frequently on equipment in food-processing plants.

Pewter is a group of alloys of tin, with varying amounts of antimony, lead, copper and zinc. The main virtue of pewter is appearance and resistance to tarnish, and it is used for table utensils.

Tin-lead solders are in common use, the usual ratio being the half-and-half solder.

The use of tin as a corrosion-resistant metal is largely confined to resisting foodstuffs and the atmosphere. Tin-coated metal cannot handle many of the conditions where the resistance of solid tin is reasonably good, since the porosity and extreme thinness of the coating on plated metal affords, at best, only a temporary protection. On the other hand the process of tinning is a simple one and cheap. In handling foodstuffs copper itself is inclined to green up and perhaps discolor the product. Although a coating of tin on the inside of copper utensils may not be permanent its advantages more than compensate for the inconvenience of an occasional retinning.

THE TIN CAN

Investigations on corrosion in the tin can have supplied a large body of information on corrosion, of general interest as well as of importance to the specialist on tin cans. For this reason the review that follows will be rather extended.

The tin can is made of tinned sheet iron, the can being formed and seamed subsequent to the tinning, and of course sealed subsequent to the filling. Though largely continuous the tin layer characteristically carries scattered pores and also possible discontinuities at seams, at which the underlying iron is exposed.

Iron itself is subject to sufficient corrosion by canned foodstuffs, either neutral or acid, that an untinned iron can would not in most cases be serviceable. Lacquered tinless cans have been the subject of experiment, with good results, over several months' time, holding beets, pumpkin and corn.¹⁹ As discussed in another chapter iron is corroded by neutral to acid solutions even in the absence of air. The corrosion goes on with hydrogen evolution and is more intense the more acid the solution. It is for this reason that a plain iron can is not satisfactory. In the presence of air or oxidizer the corrosion becomes more rapid.

Tin on the other hand is very resistant to corrosion in neutral and mildly acid solutions in the absence of air. This is due to polarization by hydrogen, by which the corrosion reaction is prevented from taking place; it is on this foundation that the tin can is serviceable. The set of data given in Table 66 illustrates the difference in resistance between tin and iron, separately, in solutions of various acids of 0.75% concentration from which air had been almost completely eliminated initially.⁶

TABLE 66.—*Tin and Iron vs. Air-free Acids.*

	Mg. per sq. dm. per day	
	Iron	Tin
Citric	5.1	.06
Tartaric	3.3	.04
Malic	4.0	.06
Oxalic	6.1	.17

TABLE 67.—*Tin and Iron vs. Air-free Fruits.*

	Mg. per sq. dm. per day	
	Iron	Tin
Grapefruit	1.8	.08
Pineapple	1.5	.11
Strawberries	2.4	.23
Blackberries	3.4	.6
Rhubarb	1.3	.32
Black sweet cherries	3.4	.26
Red sour cherries	4.5	.11

In Table 67 is another set of data comparing iron and tin in corrosion resistance, in acid food products from which air had previously been exhausted by boiling. The tests ran for 34 days.²¹

The relative attack of tin and iron is compared further in the data given in Table 68. Prior to exposure air had been exhausted from the products. The exposure period was 12 months.⁵ Polarity tests revealed that tin was anodic to iron in each of these substances. The specimens were exposed independently.

TABLE 68.—*Tin and Iron vs. Air-free Food Products.*

Product		Corrosion Rate	
		Mg. per sq. dm. per day	
		Iron	Tin
Apple—	Delicious	1.06	.019
	Paragon	1.7	.14
	Crab87	.36
	Winesap	1.9	.048
	Sweet non-such	1.4	.071
Beet—	Detroit dark red	4.0	1.08
Blackberry—	Oregon evergreen	6.2	.22
Cherry—	Bauman May	1.1	.071
	St. Medard	3.3	.074
	Napoleon	2.5	.11
	Montmorency	3.7	.095
	Blackheart	1.4	.12
	Sand	2.0	.103
Cranberry		3.9	.32
Dewberry		3.3	.30
Elderberry		1.4	.32
Grape—	Empire State	1.08	.16
	Monito86	.24
	Groff	1.4	.15
Peach—	Hiley96	.017
	Elberta	2.0	.035
Raspberry—	Ranere	2.8	.096
Rhubarb		3.0	2.1
Strawberry—	Howard 17	2.1	.22
Tomato—	Marglobe	2.1	.061

Although corrosion rates may vary with every product and every set of conditions, the three sets of data given above illustrate the typical comparison between iron and tin in air free mildly acid substances. It is true that the resistance of iron itself to most canned foodstuffs is not sufficient to make the untinned can serviceable, and that the tin can with most products is satisfactory.

Actual corrosion within a tin can would, in its early stages, be closely similar to the attack on uncoupled tin. In other words, the attack resulting from the presence of the minute cathodic areas at pores and fractures in the tin coating would be relatively immaterial until the attack of the tin progressed to the extent of laying bare considerable iron.

The rates given above for tin range from .01 to 1.0 mg. per sq. dm. per day. As an ideal and not a practical condition, an evenly distributed tin coating .0001 in. in thickness would in the case of evenly distributed attack disappear in one-half a year at a rate of 1 mg. per sq. dm. per day and in 100 years at a rate of .01 mg. per sq. dm. per day. The presence of cathodic iron areas, however, greatly increases the rate of disappearance, once these areas become greater than mere pores and cracks.

Briefly, then, the problem of tin can corrosion centers around the facts that tin is not corroded by foodstuffs in the absence of oxidizers but is corroded more or less in their presence, that iron is corroded in either the absence or the presence of oxidizers, and that iron is cathodic to tin under the conditions of the tin can. A number of other influences of importance will be mentioned later.

The tin can is successful where the amount or availability of the oxidizer that may be in the foodstuff is insufficient to strip the thin layer of tin from the iron. The iron exposed at imperfections in the tin coating is of such minute area that, cathodic as it is to the tin, it remains unattacked. Furthermore, the sacrificial corrosion of tin in consequence of its couple with a minute area of iron is immaterially small.

But products differ in their behavior in the tin can. There is the possibility even that in rare cases with some products, whose corrosive action is too rapid to make the canning of them practical, the polarity of the tin:iron couple becomes reversed, to make iron the anode. If this is in any case true—the authors have not seen good evidence of it—pinholing would be extremely rapid in the presence of oxidizer in view of the large cathodic area taking part in the reaction. Yet even though there may be no foodstuff in a tin can of such a nature that the polarity is reversed, it is a fact that some few products are too rapidly corrosive to make the tin can practical for them. Such products are characterized by being very strongly oxidizing, the consequence being that the tin is rapidly stripped and the iron left bare to attack, with a springer or perforator the result.

A good many products are reasonably satisfactory in tin cans, although of course the time over which the can remains unopened following the sealing becomes a consideration. In fact these products are border-line cases in the sense that unless precautions such as cool storage and first-grade tinned sheet are insisted upon the behavior may become unsatisfactory. Examples of such products are white and red cherries, plums, prunes, blackberries, strawberries. These products nevertheless are packed and distributed commercially and successfully.

A group of products, colored fruits, are oxidizing by virtue of the substances that give them their color. These substances are reduced in the corrosion reaction, with the result that there is a change in color. This is

of course undesirable. As a preventive these products are carried in lacquered, or enameled, tins. The corrosion problem with these is somewhat different from that of the unlacquered can, as will be discussed later.

Oxidizers. Consequential corrosion of the tin can would not take place in the absence of oxidizer. The entire difficulty comes from the unavoidable presence of oxidizer. Air itself is removed by exhaustion methods, either by heating prior to canning or by a vacuum treatment. Air is exhausted to eliminate gases that lead to excessive pressure in the can during processing, and to remove oxygen, as a preventive of corrosion. The exhaust furthermore aids in the preservation of vitamin C, since vitamin D is destroyed by oxygen when the product is processed. The air that may remain after this treatment is not serious from the standpoint of corrosion, at least in the plain can; the corrosion that takes place in using up the oxygen from this source is not damaging. In the case of the enameled can effective air exhaustion is more important.

The damaging oxidizers are those inherent in the product, such for instance as the anthocyanin pigments,^{4, 18} of colored fruits and berries. Some products, as already stated, are so strongly oxidizing that they cannot be handled at all in tin cans, other products that lose their color in plain cans are too strongly oxidizing to be satisfactory in enameled cans, since the full effect of the oxidizer is concentrated at the small areas exposed at breaks in the enamel.

Polarity. A good many tests in food products have demonstrated that, in exposure to them, iron is cathodic to tin. In fact, aside from the momentary reversed polarity at the time the couple is first immersed the only data the authors have seen which demonstrate that a foodstuff may produce reversed polarity as an equilibrium condition have referred to canned corn in the presence of air, in one test.²⁸ It is unlikely that this condition is normal to canned corn, however. Kohman and Sanborn²⁵ have stated that tin was found to be cathodic to iron in some lots of dried prunes.

On the other hand iron has assumed an anodic position in dilute hydrochloric carrying stannous ions, whereas in the more concentrated range and in hydrochloric without added stannous ions the iron was cathodic.²² Behavior in the dilute solutions, in which iron appears to be anodic, is given in Table 69.

TABLE 69.—*Tin:Iron Couples vs. Hydrochloric Acid Containing 10 p.p.m. of Tin as Stannous Chloride.*

Acid Strength %	Hours Exposure	Loss in Milligrams			
		No Contact		Contact	
		Iron	Tin	Iron	Tin
.05	308	11.6	2.7	12.9	0.6
.10	235	23.2	3.2	47.6	0.7

Iron also has assumed the anodic condition in a couple where oxygen or hydrogen was bubbled at the tin electrode, without similar agitation at the iron electrode. Where gas was bubbled at both electrodes or only at the iron, the iron was cathodic.²⁶ It has been reported that either electrode may be made cathodic by gently bubbling air around it.²¹ Finally, iron has been found anodic in .01 normal sulfuric acid of pH 1.81.¹⁴ It is well recognized, that under the conditions of the tin can, tin is normally anodic to iron.

The direction and intensity of current flow in a galvanic couple is largely dependent on the relative concentration and nature of the metal ions against the two electrodes. The rate of removal of stannous ions from the vicinity of corroding tin is a factor of importance to which attention has been called by a number of investigators.^{2, 6, 11, 14, 22} Some foodstuffs withdraw stannous ions from solution more rapidly than others, an effect favoring at once more rapid corrosion of the tin and a more anodic position towards iron. It has been observed that the building up of stannous ion concentration has actually caused a reversal of polarity by which iron is thrown anodic, in dilute hydrochloric acid solutions,²² as already noted.

The relative overvoltage character of tin and iron has been offered as a factor by which tin is maintained anodic to iron.²⁶ Tin has a notably high overvoltage, a fact that is important in suppressing the natural uncoupled corrosion of tin in the absence of air. Furthermore the high overvoltage of tin suppresses the corrosion of iron coupled with tin, when the iron is anodic to the tin. The overvoltage of tin becomes more important as the oxidizing capacity becomes less. It is difficult to understand the suggestion that the high overvoltage of tin is the cause of the tin being anodic to iron within the tin can. It does not necessarily follow that tin becomes the anode because it cannot function as a cathode.

It has been demonstrated that soluble tin salts—stannous ions—suppress the normal corrosion of iron.^{6, 14, 29} According to the tests of Kohman and Sanborn²³ the reason for this lies in the fact that stannous ions increase the overvoltage of iron. The effect of this on the galvanic currents of a tin:iron couple would be expected to be suppressive, since the cathodic activity of iron is lowered. It is likely that this factor becomes important in those cases where there is sufficient stripping of the tin to bare an area of iron that if cathodically active would materially hasten the anodic attack of the remaining tin.

The exposed area of iron in a freshly packed can is extremely small. It is likely that where cathodic (the normal if not invariable condition) it is completely protected. In other words no local corrosion independent of the couple is likely to take place on the iron. On the other hand, if the product is oxidizing to the extent that tin becomes stripped over relatively large

areas, local action will take place on the iron long before the tin is entirely stripped. This local action, if the oxidizer is not used up in stripping the tin, will eventually manifest itself in perforation and, if little or no oxidizer remains, in a springer. What seems to be contradictions to this may sometimes occur. Thus a perforation may result when little or no oxidizer remains. The general principle, however, is sound.

Tin stands in a more noble position than iron in the ordinary electrochemical series appearing in text books. It is well recognized, however, that the electrochemical behavior of metals in couple is controlled by factors that do not necessarily exist in the test conditions under which this series is obtained. As mentioned above, tin, though characteristically anodic within the tin can, is cathodic to iron under some conditions. It has been stated more than once that in atmospheric exposure tin is cathodic. Yet lacking definite proof of this, the rusting of tin plate in the atmosphere may fully as well be a case of the absence of protection from tin as the presence of galvanic currents in which tin acts cathodically. But tin has been shown cathodic to iron for instance in water ^{7, 27} and in salt solutions.⁷

Effect of acidity. In acidity canned food products range from a pH of about 2.4 for the most acid fruits to a pH of about 7.

It is natural to expect acidity, or hydrogen-ion concentration, to be a factor determining the corrosiveness of foodstuffs. Contrary to expectations, perhaps, the fruit products of lesser acidity (pH 4 to 5) give greater trouble from corrosion than those of greater acidity (pH 2.4 to 3.4).

One reason for this seems to be that there is more effective removal of tin ions from solution in low acidity products,^{4, 11} a factor that promotes the corrosion of tin either in couple with iron or not.

Probably the more important reason is that demonstrated by Kohman and Sanborn,²⁴ namely, the more anodic nature of tin, in relation to iron, in the more acid substance. For example the relative weight losses of tin and iron samples in couple in dried prunes of a pH of 3.75, as compared with the losses in dried prunes to which citric was added to give a pH of 3, were as shown in Table 70.

TABLE 70.—*Tin and Iron vs. Dried Prunes.*

pH	Mg., loss	
	Tin	Iron
3.75	6.5	12.2
3.	25.1	2.3

The greater attack on the tin and the less attack on the iron, at pH of 3, are the important facts in this comparison. The implication in this comparison is that as iron becomes bared within the can, corrosion of the iron will take place in the case of the more acid product only after a greater area of iron

becomes exposed, because of the greater protective force of the anodic tin. The fact that the total corrosion is greater in the more acid product may not be important, as suggested by the results given in the next paragraph.

In a practical test, after about nine months cans of ordinary dehydrated dried prunes with a pH of 3.95 had 90% can failures, whereas, cans carrying the same product with citric acid added to give a pH of 3.80 suffered no failure.²⁵

It has been found further ²⁹ that the addition of 0.3% citric acid to syrups used in packing both black and white cherries and 0.5% acid to syrup used for prunes has led to a suppression of corrosion. In the case of plain cans the prunes were very much less corrosive, and in the case of lacquered cans all three products were very much less corrosive. As an example, in a 7-month storage period 77% of the cans holding prunes became hydrogen swells in the case of no added acid, and none became swells with the added acid, both in plain and lacquered cans. The color and flavor of the contents were improved by the acid addition.

It does not seem to have been demonstrated that increasing the acidity of a food product suppresses its oxidizing capacity, yet this would seem a possible contributing factor towards the lessened corrosion activity. Ferrous ions have been shown to be oxidized far more readily to ferric in the less acid concentrations of the range pH 2.41 to pH 5.04.²⁹

Nevertheless it remains true that in pure acids free or nearly free of oxidizer, other things being equal, iron corrodes faster with increasing hydrogen-ion concentration. It is conceivable that insofar as tin corrodes in a tin-iron couple by hydrogen evolution at the iron anode, the more acid solution would give a more intense action.

According to tests of Morris and Bryan, tin corroded more rapidly with increasing hydrogen-ion concentration, in citric acid solutions of pH 2.4 to pH 5.5 in the presence of air.

Temperature. The temperature at which tin cans are stored, in the case of all corrosive products, becomes an important factor in behavior. Kohman ¹⁷ has stated that, with fruits, losses due to springers and perforators increase from a negligible figure at 32° F. to a very high figure at 97° F. An excellent comparison in behavior of cans of berries stored at 50° F. and others at 70° F. is given in Figure 23 arranged ²⁹ from the tests of Kohman.¹⁷

Enameled Cans. Enameling the inside surface of cans prevents discoloration or decoloration of some products and prevents the unsightly blackening of the tin surface in the case of other sulfur-bearing products.

The coloring matter in many fruit products that may be affected is oxidizing to the extent that it enters the cathodic corrosion reaction. It is in this reaction that their change in color takes place. It has been observed that products that have become decolorized in the can regain their color when again exposed to the air.^{18, 29}

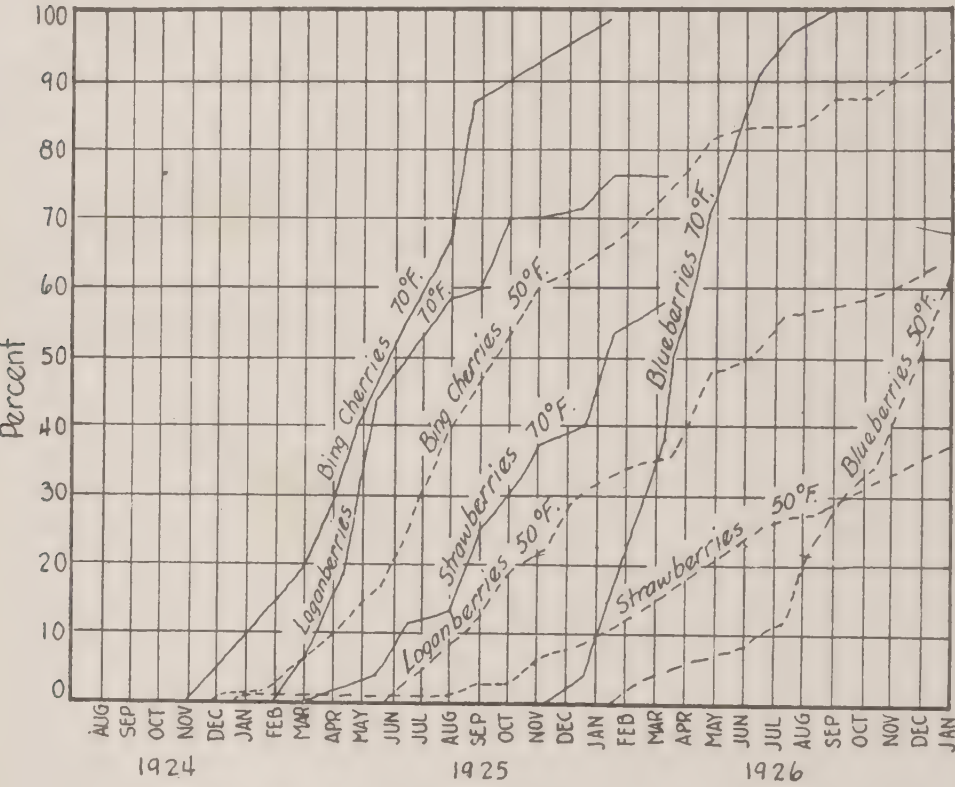


FIGURE 23. Failures Due to Hydrogen Swells and Perforations in Storing Canned Fruits.

Where tin is exposed at ruptures or imperfections in the enamel obviously corrosion will take place. It is common experience that enameled cans are more susceptible to destructive corrosion than plain cans,^{20, 29} the reason being that the full oxidizing capacity of the contents is concentrated in its effect at the breaks in the enamel. Whereas, in a plain can the oxidizer may largely be used up before the tin is stripped, in the enameled can this is much less likely in view of the small area of tin to be stripped.

Kohman and Sanborn²⁴ believe that tin in an enameled can corrodes faster because iron, being in larger area relative to the tin than in the case of a plain can, is more effectively cathodic. In other words, the galvanic corrosion of tin is more severe because it is concentrated on a lessened area of tin.

They also point out that in an enameled can the tin ions are in less quantity and consequently their inhibitive effect on iron corrosion is less.

Once the tin is stripped at breaks in the enamel corrosion of the iron takes place, both with hydrogen evolution and—if oxidizer remains—without important hydrogen evolution. It has been recorded¹⁸ that in the case of apples with oxygen in plain cans the oxygen disappears quickly and the hydrogen is slow to form. Yet in enameled cans the oxygen is slow to go and then the hydrogen forms rapidly. This is of course what would be expected.

Enameled cans, as stated, are more likely to suffer destructive corrosion than plain cans.* The corrosion may lead either to a springer or a perforator. Kohman and Sanborn²⁵ have observed that the action of fruits in enameled cans is localized, and frequently the can becomes perforated without sufficient hydrogen being formed to destroy the vacuum in the can. This is characteristic, they say, of low-acid fruits, whereas high-acid fruits in enameled cans generally cause losses by bulging the can end rather than perforating.

It should be kept in mind of course that enameled cans are widely and satisfactorily used in spite of occasional failures with some products.

Tin pickup and toxicity. It is now generally agreed among those who have gone into the matter that tin as it occurs in foodstuffs is physiologically inactive. It would be a difficult matter to get representative figures showing to what extent tin occurs in canned foods at the present time, since tin determinations by regulatory officials and others are infrequent.

A set of data from Kohman, quoted by Morris and Bryan,²⁹ has given the quantities of tin in the can contents given in Table 71.

TABLE 71.—*Tin Pick-up in the Can.*

	P. p. m.			
	1½-5 Months		10½-13 Months	
	Max.	Min.	Max.	Min.
String Beans	97	75	220	154
Corn	13	3	—	—
Peas	32	9	26	12
Pumpkin	82	31	476	44
Tomatoes	175	42	148	58
Apples	166	34	203	27

Inhibitors and accelerators. Mention has already been made of the effect of tin ions in increasing the overvoltage of iron and so suppressing hydrogen evolution from iron either uncoupled or coupled with tin. Mention

* An exception is sauerkraut, in which hydrogen springers occur more rapidly in plain cans than in enameled.

has also been made of the withdrawal of tin ions from solution by substances in food products, and the consequent greater attack of tin. There has been observed²² an increased corrosion of tin brought about by apple pomace, egg white, casein, gelatin, crushed peanuts, crushed almonds, crushed prune kernels.

The effect of the addition of apple pomace to acids on the corrosion of iron and tin is covered in the data given in Table 72.²² Air was exhausted from the substances by boiling before testing and the specimens were exposed 210 hours at room temperature.

TABLE 72.—*Tin:Iron Couples vs. Acids.*

Substance	Corrosion Rate—Mg. per sq. dm. per day					
	Iron			Tin		
	Alone in Bottle	In Bottle with Tin, No Contact	In Contact with Tin	Alone in Bottle	In Bottle with Iron, No Contact	In Contact with Iron
Citric acid						
Without pomace.	26	3.9	1.8	.5	.57	.62
With pomace ...	2.4	2.8	.62	1.2	.80	4.6
Malic acid						
Without pomace.	12	2.3	2.5	.68	.63	.55
With pomace ...	2.2	2.3	.97	.68	.63	2.1
Acetic acid						
Without pomace.	11	5.5	7.6	.93	.63	.06
With pomace ...	2.9	3.0	5.8	.11	.23	.66
Malonic acid						
Without pomace.	34	6.4	13	.74	.63	.49
With pomace ...	2.9	3.3	2.9	1.3	1.1	1.6
Succinic acid						
Without pomace.	16	5.8	11	.60	.51	.11
With pomace ...	2.2	2.2	1.6	.22	.17	.57

The pomace suppressed the corrosion of iron alone, much as the tin ions did. In the tests where iron and tin specimens were uncoupled in the same containers there was a time lapse following the start of the test before the tin-ion concentration had built up, so that tin ions alone may have been a more effective inhibitor than pomace alone. In the presence of both tin ions and pomace the inhibitive effect of the two was not cumulative. Pomace had a variable effect on tin alone, but was strongly accelerating in every case with coupled tin and correspondingly inhibitive with coupled iron.

In .5% citric acid the addition of 15 to 50 parts per million of tin ions (as citrate) lessened the corrosion of iron to a rate one-third to one-seventh of what it was without the tin ions.²⁹

Morris and Bryan²⁹ have considered extensively the question of inhibitors and accelerators, and have called attention particularly to the effect that sulfide-sulfur compounds have in throwing iron much less cathodic if not actually anodic to tin.

Containers Ordinarily Used for Food Products. Table 73, prepared by the Research Department of the American Can Company, lists the containers ordinarily used with different foodstuffs. The table carries as well the approximate pH value of each product.

"Two types of enamel are in common use, both a golden yellow. One type (sanitary enamel) is used to prevent the bleaching of red fruits and also to protect the tin coating. The other (C-enamel) is used to prevent discoloration of the contents and the staining of the inside of the can such as occurs with some vegetable and meat products when packed in plain cans. Some foods contain sulphur and under heat this sulphur discolours the tin plate for the same reason that it discolours a spoon left in contact with a cooked egg. The stain is harmless but unattractive."

TABLE 73.—*Containers Ordinarily Used.*

Product	Approx. pH	Containers ordinarily used
<i>Acid Fruits and Vegetables (Sanitary Enamel)</i>		
Apple Butter	3.9	Plain
Applesauce	3.4	Plain
Apples	3.3	Plain
Apricots	3.2	Plain
Beets	5.3	Sanitary Enamel
Blackberries	3.3	Sanitary Enamel
Blueberries	3.7	Plain
Cherries, (except Royal Anne)	3.4-3.8	Sanitary Enamel
Cherries, Royal Anne	3.8	Plain and San. Enamel
Cranberries	2.6	Sanitary Enamel
Cranberry Sauce	2.6	Sanitary Enamel
Gooseberries	3.0	Plain
Grapefruit	3.5	Plain
Grapefruit Juice	3.4	Plain
Orange Juice	3.6	Plain
Pickles, Dill	3.9	Plain and San. Enamel
Pickles, Sour	3.5	Plain and San. Enamel
Pumpkin	5.0	Sanitary and C-Enamel
Prunes, Pureed	4.0	Sanitary Enamel
Pimientos	4.7-5.1	Plain
Peaches	3.5	Plain
Pears	3.9	Plain
Raspberries	3.6	Sanitary Enamel
Rhubarb	3.2	Sanitary Enamel
Sauerkraut	3.6-4.1	Plain and San. Enamel
Strawberries	3.4	Sanitary Enamel
Tomatoes	4.2-4.5	Plain and San. Enamel
Tomato Juice	4.2-4.5	Plain and San. Enamel
Tomato Soup	4.7-5.3	Plain
Tomato Pulp	4.2-4.5	Plain

Product	Approx. pH	Containers ordinarily used
<i>Non-Acid and/or Sulfur-bearing Products (C-enamel)</i>		
Asparagus, White	5.6	Plain and C-Enamel
Asparagus, Green	5.6	Plain
Artichokes	varies	Plain
Beans, Greer	5.3	Plain
Beans, Wax	5.3	Plain
Beans, Lima	5.9	Plain and C-Enamel
Beans, Kidney	5.8	Plain and C-Enamel
Beans, Pork and Beans	4.6-5.2	Plain
Carrots	5.0	Plain San. and C-enamel
Corn	6.3	C-Enamel
Figs	4.9	Plain and C-Enamel
Hominy Lye	7.0	Plain and C-Enamel
Okra	4.9	Plain
Onions	5.3	C-Enamel
Peas	6.2	Plain and C-Enamel
Potatoes, Sweet	5.4	Plain and C-Enamel
Potatoes, White	5.9-6.2	Plain
Spaghetti	4.8-5.4	Plain
Spinach	6.2	Plain
Succotash	6.0	C-Enamel
Turnip Greens	6.2	Plain

Marine Products

Clams	6.6-6.8	C-Enamel
Clam Cakes	6.4	C-Enamel
Clam Chowder	6.2-6.5	C-Enamel
Clam Juice	6.6-6.8	C-Enamel
Clams, Minced	6.6-6.8	C-Enamel
Crabs, Plain	6.9-7.7	C-Enamel
Lobster	6.6-6.8	Plain and C-Enamel
Oysters	6.6	Plain and C-Enamel
Salmon	6.1-6.6	Plain
Shrimp	6.8-7.0	C-Enamel
Tuna	6.0	Plain

Meat Products

Beef, Corned	6.2-6.3	Plain
Chicken, Deviled	6.3	Plain and Enamel
Chicken, Whole, Half, Sliced	6.0-6.3	Plain and Enamel
Chili Con Carne	4.7-6.0	Plain and Enamel
Frankfurters	6.3	Plain
Ham, Deviled	6.3	Plain
Ham, Spiced	6.3	Plain
Ham, Whole	6.3	Plain
Sausage, Vienna	5.9-6.3	Plain
Tamales	varies	Plain
Tongue, Lunch	5.8-6.0	Plain and Enamel
Tripe	6.2	Plain

ACIDS

Briefly, tin is inherently only moderately resistant to ordinary acid solutions in the presence of air. Rates of corrosion are such that though block tin might often give a reasonably good life, a tin coating would rapidly disappear—typically in a very few days of continuous exposure. In the absence of air in dilute acids, however, tin is very resistant, such that a tin coating will persist over a year and more of continuous exposure. This latter subject has already been discussed in the paragraphs on the tin can.

The reason for the good behavior of tin in air-free, dilute acids lies in its high overvoltage. It becomes polarized by hydrogen on first exposure, this hydrogen preventing the flow of the currents that must accompany corrosion and thereby actually prohibiting further corrosion. Oxidizers in the acid, either as dissolved oxygen or as some other substance, will depolarize the hydrogen and allow corrosion to proceed.

Quantitative expression of the acid attack of tin will be given in the data following. It will be seen that acid solutions of low air content or of virtually no air content corrode tin at rates of 3 to <1 mg. per sq. dm. per day. If the acid is in moderately concentrated solution, though airfree, the rates become much higher. The reason for this is that the force of the reaction by which the hydrogen plates out becomes great enough, with increasing hydrogen-ion concentration, actually to evolve hydrogen. The polarization by hydrogen, consequently, will no longer prevent further corrosion.

Furthermore where the solutions become aerated or, like nitric, are otherwise oxidizing the rates are more on the order of 500 mg. per sq. dm. per day. Elevated temperatures are normally accelerating.

In Table 74 are figures which point out clearly the accelerating effect, on the corrosion of tin, of dissolved oxygen. In one set of tests the acids

TABLE 74.—*Tin vs. Acids.*

Acid	Conc. %	Mg. per sq. dm. per day	
		Hydrogen Gas	Oxygen Gas
Nitric	3	630	640
Hydrochloric	6	60	11,100
Sulfuric	6	35	4,300
Acetic	6	15	2,300

were saturated with hydrogen gas, and in the other with oxygen. The solutions were moderately concentrated and consequently sufficiently high in acid that even when oxygen-free they were corrosive.³⁴ It is to be noted that in the case of nitric, oxygen did not increase corrosion, the reason of course being that nitric acid itself is oxidizing.

The data in Table 75 were obtained in tests in which tin specimens were partially immersed in quiet acids held in sealed containers. The degree of

TABLE 75.—*Tin vs. Acids.*

Acid	Temp. ° F.	Duration	Mg. per sq. dm. per day
Hydrochloric—1%	70	5 days	50
Sulfuric—1%	70	"	15
Acetic—1%	70	"	13
Citric—0.2%	70	"	18
Lactic—1%	70	"	18
Butyric—1%	70	"	+
Lactic—1%	145	5 hours	96
Butyric—1%	145	"	4

aeration was consequently low. The acids, with the exception of butyric, were probably strong enough to cause some hydrogen evolution.¹⁵

Hydrochloric and sulfuric acid solutions that had been air-exhausted prior to test gave the results in Table 76. The tests were made at 68° F.²²

TABLE 76.—*Tin vs. Air-free Acids.*

Conc. %	Hours Exposure	Mg. per sq dm. per day	
		Sulfuric	Hydrochloric
20	1	290	190
10	1	36	72
5	1	48	36
1	1	24	36
1	10	10.8	6
.5	10	14.4	10.8
.1	10	13.2	7.2
.05	10	8.4	14.4

It is to be noted that in concentrations as low as .05% the action was marked. Most if not virtually all of the corrosion was accompanied by hydrogen evolution, assuming that air was effectively exhausted and that the removal of hydrogen gas from the surface by dissolving in the acid was relatively slight.

It has already been stated that essentially air-free acids in dilute to very dilute solutions are only faintly corrosive. An illustration of this fact is given by tests²⁹ of 28-days duration in air-free .5% citric acid solution of pH of 2.41 and the same solution buffered with sodium citrate to various pH values up to a pH of 5.5. The rates were .2 mg. per sq. dm. per day or less. These same solutions in the presence of a limited supply of air gave rates of 10 to 15 mg. per sq. dm. per day.

Likewise rates in 210-hour tests²² in air-exhausted 0.75% malic acid, and other acids of equivalent strength, at room temperature, were as shown in Table 77. The exposure period was 210 hours.

TABLE 77.—*Tin vs. Air-free Acids.*

	Mg. per sq. dm. per day
Citric5
Malic68
Acetic93
Malonic74
Succinic.60

An important point in considering the effect of dilute air-free acids on tin is the influence of tin compounds in the solution towards suppressing attack. This has been mentioned earlier in connection with corrosion of the tin can, yet at this point expression of the principle is useful. In one set of tests hydrochloric acid solutions were used, in the other hydrochloric acid with an added 10 parts per million stannous ion. In all tests the acid was air-exhausted.²² (See Table 78.)

TABLE 78.—*Tin vs. Hydrochloric Acid.*

Hydrochloric Conc. %	Without Stannous Ion		With Stannous Ion	
	Duration Hours	Mg. per sq. dm. per day	Duration Hours	Mg. per sq. dm. per day
20	1	190	1	275
5	1	36	1	36
1	1	36	1	12
.25			139	.3
.10	10	7.2	235	1.6
.05	10	14.4	308	1.0

In the case of the more dilute solutions the presence of the stannous ions makes the difference between quite appreciable corrosion and negligible corrosion. Translated into terms of tin can corrosion it would be the difference between rapidly destructive corrosion and permissible corrosion. The question is an important one in view of the fact that stannous ions, no matter how slight the corrosion, are introduced into the solution in the diffusion layer against the metal. If for any reason the stannous ions are effectively removed, as by stirring or, as in a tin can, by absorption by the foodstuff, the suppressing effect is not felt.

In interpreting the tests quoted immediately above, the fact should not be overlooked that corrosion in the acid to which stannous ions were not previously added was in itself introducing stannous ions; their concentration, however, could not have built up to the full suppressive effect of the other acid.

Strongly acid solutions, as already stated, will corrode tin even in the absence of air. Corrosion with these is accompanied by hydrogen evolution, the tendency to corrode being greater than the counteracting force of over-voltage. Thus in the absence of oxygen³⁴ a 6% hydrochloric acid solution (very strong acid) gave a rate of 550 mg. per sq. dm. per day, and a 6% acetic acid (a weak acid) a rate of 14 mg. per sq. dm. per day.

A .5% air-free citric acid solution, having a pH of 2.4, failed to be corrosive.²⁹ One of the more significant sets of tests indicating the boundary between the acidity range that is not corrosive, because of the preventive effect of overvoltage, and the range where the corroding tendency is powerful enough to overcome overvoltage, is that of Culpepper and Moon.⁶ These investigators held various acid solutions, from which air had previously been exhausted, in tin cans for a year, the solutions ranging from a pH of 3.56 to a pH of 0.79, as follows:

	pH range
Oxalic	2.96-0.79
Citric	3.44-1.81
Malic	3.42-1.57
Tartaric	3.56-1.57

Within the pH range of 1.80 to 1.60 the oxalic, malic and tartaric solutions passed from a condition of being non-corrosive or only very slightly corrosive, to one of very definite corrosiveness. In the more dilute range the cans did not suffer failure, in the more concentrated the cans did fail. The cans holding citric did not fail, but with this acid the pH values did not enter the range shown to be corrosive in the other acids. Of course the presence of tin:iron couples and of tin ions introduced complications of an indeterminate nature, yet the results are of some significance.

FOOD PRODUCTS OTHER THAN IN THE TIN CAN

It already has been pointed out that acid solutions in the free presence of air are mildly to severely corrosive. Food products, even though many of them are acid, are handled to some extent in tin or tin coated equipment. One example of this is the common heavily tin-coated milk can and the tin-coated copper tubing of dairy equipment. Another example is the heavily tin-coated copper cooking utensils used in the galleys of ships and in hotel kitchens. The heat transfer efficiency of these is good, thanks to the copper. The tin on the inside surface of the utensils is a preventive of the greening and discoloration that result from copper with many foodstuffs.

Milk, though a distinctly acid product, has only slight action on tin, even when the milk is strongly aerated. For instance, specimens of block tin exposed on the tubes of a surface cooler handling sweet milk were affected as shown in Table 79.¹⁶

TABLE 79.—*Tin vs. Milk (Surface Cooler).*

Temp. ° F.	Mg. per sq. dm. per day
143	3-0
79	3.8-3
63	3.1-1.5
43	3.1-1.5

In another case the maximum corrosion rate of four specimens exposed to agitated milk for 30 minutes at 167° F. was 8 mg. per sq. dm. per day.³¹

Hunziker and co-workers¹⁵ obtained the data in Table 80 from partial immersion tests in sealed containers:

TABLE 80.—*Tin vs. Quiet Milk.*

Product	Temp. ° F.	Duration	Mg. per sq. dm. per day
Sweet milk	70	5 days	1.5
	145	5 hours	6.7
Sour milk	98	5 days	2.4
	70	2 days	1.1
Sweet cream	70	5 days	.17
	145	5 hours	11
Sour cream	70	5 days	.61
	145	5 hours	6.7
Sour neutralized cream	145	5 hours	11

Tin exposed in evaporators, at 140° to 148° F. and 25 in. vacuum, producing evaporated and condensed milk respectively, corroded at the rates in Table 81.¹⁶

TABLE 81.—*Tin vs. Milk (Evaporator).*

Location	Mg. per sq. dm. per day	
	Evaporated Milk	Condensed Milk
Above liquid surface	< 6.5	< 2
At liquid surface	< 5	
Below liquid surface	< 9	< 3

The action on tin of fruit juices in the free presence of air is perhaps greater than that of milk. A range of rates from 1 to 25 mg. per sq. dm. per day is probably typical for tin in quiet and mildly aerated fruit juices at room temperature.

Hot fruit juices, on the other hand, are strongly corrosive, as indicated by the data in Table 82.³⁰ The specimens were exposed in the boiling juices for 24 hours.

TABLE 82.—*Tin vs. Boiling Fruit Juices.*

	Mg. per sq. dm. per day
Tomato juice (10 hours)	220
Apple juice	350
Lemon juice	128
Red grape juice	300

ALKALINE SOLUTIONS

Tin has fair to poor resistance against caustic alkaline solutions. Like aluminum, tin forms double compounds with alkalis; though the reaction is not nearly so rapid as in the case of aluminum, tin is not suitable for

handling these. Mantell²⁸ has stated that tin is readily attacked by alkaline cosmetic pastes. Tests by Hale and Foster¹³ have given the data in Table 83; the specimens were quietly submerged in 0.8% sodium hydroxide at 68° F.

TABLE 83.—*Tin vs. Sodium Hydroxide.*

Duration of exposure	Mg. per sq. dm. per day
7 days	43
28 "	18

Warts and Whipple³³ found corrosion of the same order by 4% sodium hydroxide at 98° F. in 45-days exposure.

Dilute aqueous ammonia, it appears, is not corrosive to tin. A .7% solution failed to attack tin at room temperature over a 28-day period.¹³ Other than this result no data seem to be available.

SALT SOLUTIONS

Salts whose solutions are acid in reaction attack tin in the presence of air or other oxidizer. Strongly oxidizing salts like ferric chloride are rapidly corrosive; salts like aluminum chloride are strongly corrosive when aerated, less so when of low aeration.

Neutral and mildly alkaline reacting salt solutions are moderately low in corrosive action on tin. A number of rates are given in Table 84,¹³ covering quiet submersion at 68° F.

TABLE 84.—*Tin vs. Salt Solutions.*

Salt Solution	Mg. per sq. dm. per day	
	7 days	28 days
Sodium chloride—1.3%	< 1.4	2.7
Magnesium chloride—0.9%	23	3.6
Calcium chloride—1.1%	19	2.7
Sodium carbonate—1.0%	1.4	< 0.4

Though block tin would be serviceable under such conditions, tinplate would be expected to be short lived when it is considered that a rate of 1 mg. per sq. dm. per day corresponds to a penetration rate of .0002 in. per year.

TABLE 85.—*Tin vs. Alkaline Solutions.*

Added Alkali	Mg. per sq. dm. per day
Sodium phosphate—0.1%	8
" " —0.5%	2.5
Sodium carbonate—0.1%	9
" " —0.5%	2.1
Sodium hydroxide—0.1%	7.2
" " —0.5%	0
Calcium " —0.1%	4.0

In Table 85 are rates in a very dilute hypochlorite solution carrying 255 parts per million available chlorine, with additions of alkalis;³² the tests ran for 25 days at ordinary temperature. These rates in very dilute hypochlorite are low to negligible. Alkaline hypochlorite solutions of moderate concentrations are rapidly corrosive to tin.

WATERS

The good resistance of tin to waters is responsible for certain uses. One of these is in equipment handling distilled water. The rate of metal absorption from solid tin lining and tubing is very low, perhaps as low as for any metal. The structural limitations of tin prevent full appreciation of this resistance.

Tin exposed 4 years to sea water, with total submersion 93% of the time, was tarnished and pitted in spots to a depth of .020 inch (25 mg. per sq. dm. per day).¹⁰ Tinned copper hung in the hot end of a condenser handling Hudson River water of low velocity and at temperatures up to 200° F., had lost much of the tin coating in a month's time.¹⁶

Carbonated water is stated to have practically no corrosive action on tin.²⁸

ATMOSPHERE

Tin is one of the more resistant metals against the atmosphere; it is reasonably resistant to tarnishing. This is true of industrial as well as of ordinary atmospheres. Yet in sea atmospheres corrosion may be fairly active, with development of encrusted salts.⁸ This non-tarnishing property is not widely important, however, since in sheet form tin is too expensive and too low in strength to make it useful as a roofing or decorative material, and the lack of permanency that is characteristic of tin plate in common with many other plated materials prevents it from being useful when unprotected by paints. Painted tin plate is used to a limited extent, however; Terne plate, in which the plate is an alloy of lead and tin is a very commonly used material.

HIGH-TEMPERATURE GASES

Lack of tenacity limits the usefulness of tin to below about 400° F., even though oxidization rates up to this point are negligible. An exception is the use of fusible pure tin plugs for boilers, whose function is to melt when the boiler becomes overheated, and thus release the pressure. Cases of corrosion and oxidation of these plugs in use in such a way that they become infusible have been studied.^{3, 9, 12} This condition was found to be related to a too-high impurity content of zinc and to attack of water that had infiltrated from the boiler to the fire end of the plug.

TIN AND TINPLATE

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Chapter X

Lead

Corrosion resistance,²⁶ is the most important factor in the industrial use of metallic lead; the satisfaction given by lead cable sheathing, piping, roofing, and acid-handling equipment depends on this property, together with low cost and workability. Certain other uses are based on the low melting point or the high specific gravity of lead. The comparatively low structural strength and softness of lead, advantageous for some purposes, prevent even wider application in the sphere of corrosion resistance.

In this country lead is furnished in several varieties. "Chemical" lead is a relatively pure product, and is often spoken of as "soft lead"; it carries less than 0.1% of other metals, mainly copper. "Hard" lead, in which up to 15% antimony is the hardener, is used to a considerable extent where a stronger material than "soft" lead is desired. Hard lead under a few corrosive conditions only is less resistant than the purer grade. Other hardeners than antimony are sometimes used, such as calcium, cadmium, and tin. Lead with .06-.08% tellurium is a commercial product with greater strength and fatigue resistance than ordinary lead.^{46, 47} Cable sheathing, a very large use for lead, is made commonly of 1% antimony lead, or 3% tin lead, sometimes of soft lead, and recently to some extent a lead carrying a few hundredths of 1% of calcium as a strengthener.

Soft solders consist of lead and tin in varying proportions, usually about half-and-half. Lead further is a constituent in greater or lesser degree in friction bearing alloys.

CORROSION RESISTANCE—GENERAL

Elemental lead is one of the metals that easily replaces hydrogen in aqueous solution, behaving in this respect more like iron than like copper. As a corollary the reactivity of lead in aqueous solutions is inherently rather pronounced. That lead has a commercial degree of corrosion resistance in many types of aqueous solution is due to the suppression of its natural reactivity by the development of protective films of corrosion products. So effective are these films at times that the actual equilibrium corrosion rate

of lead may be very low, as in exposure to dilute sulfuric acid solutions or to the atmosphere. A good example of the permanence of lead is the case of lead water pipe dug up in Italy after burial for nineteen centuries.

The chemistry of the corrosion of lead by aqueous solution, therefore, involves the problem of the relative solubilities of lead compounds and the physical characteristics of the compounds as they exist in the solid state. Since it has not been customary in corrosion investigation to approach the subject through analyzing the chemistry and physico-chemistry of the corrosion products, the present-day knowledge of the resistance and corrodibility of lead consists largely of empirical data. There appears, however, a definite relation between service behavior and certain items in the solubility values listed below. The figures in Table 86 represent solubility in parts per 100 parts of water.

TABLE 86.—*Solubility of Lead Compounds.*

	<i>Solubility</i>		<i>Solubility</i>
Acetate	Very high	Oxalate00016
Carbonate	Very low	Oxide	Very low
Chloride673	Oxide, hydrous	Very low
Chromate	Very low	Phosphate000014
Fluoride064	Sulfate	Very low
Formate	1.6	Sulfide0001
Iodide012	Sulfite	Very low
Nitrate	54.3		

Lead generally has good resistance to neutral solutions, where lead carbonate and possibly oxide are corrosion products, and poor resistance to alkaline solutions in which these are soluble. Experience has shown as well that lead is commercially resistant to chromic, sulfuric, sulfurous, and phosphoric acids; that it is attacked at somewhat higher rates by hydrochloric and hydrofluoric acids; and that it is strongly corroded by acetic, formic, and nitric acids. Also, nitrate salt solutions are moderately corrosive whereas carbonate solutions are not.

Protective layers of corrosion product form on lead in a rather broad neutral range of aqueous conditions. Corrosion products become less protective as the solution becomes either strongly acid or strongly alkaline. A rough idea of the boundaries of the neutral range may be gained by reference to Figure 24. These results³ were obtained in tests in which lead specimens were held for periods up to 30 days in stoppered bottles. Though the curves may shift somewhat under exposure conditions differing from this, these results are of great value in suggesting the extent of the neutral, relatively non-corrosive range of solutions. Of course some strong acids, notably sulfuric and phosphoric, develop corrosion product layers on lead that suppress corrosion to rates far below those indicated for acetic and nitric.

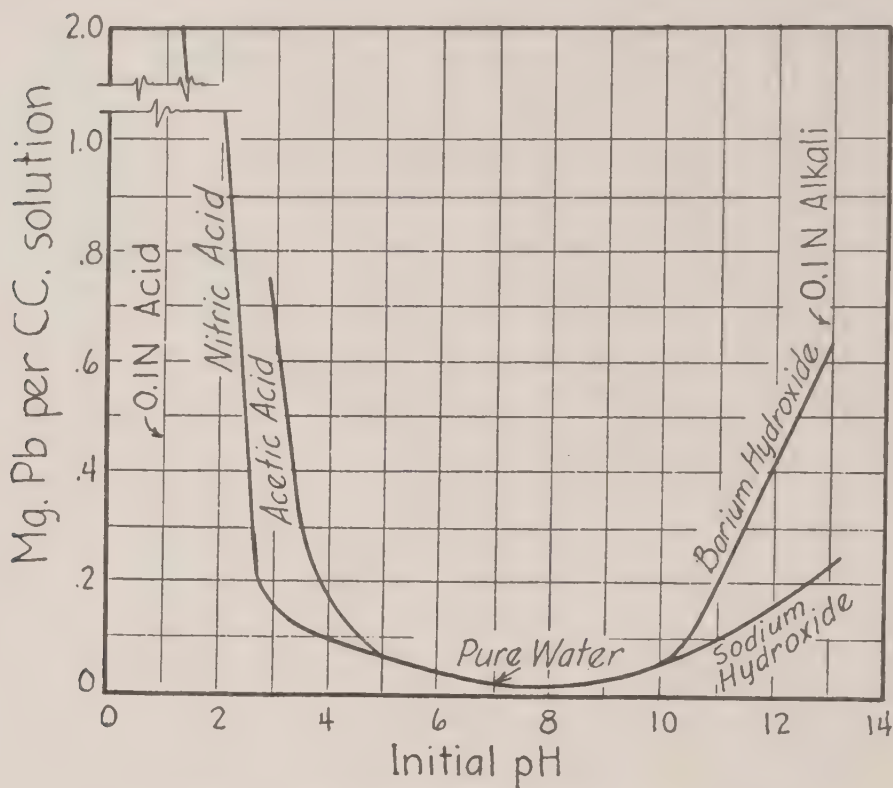


FIGURE 24. Effect of pH Value on Corrosion of Lead.

EMBRITTLEMENT

Lead sheet and cable sheathing at times have failed by cracking in a manner that has suggested intercrystalline embrittlement.^{5, 23, 24, 41, 42, 44, 49} The investigations of Beckinsale and Waterhouse⁵ have strongly suggested the importance of stress, especially vibration stress, as a factor promoting failure. The intensity of stress required is low, in view of the low elastic limit and strength of lead.* Later considerations of Haigh and Jones²⁴ seem conclusively to show that penetration of oxygen is the necessary corrosion environment favoring fracture, and that simple atmospheric exposure in the presence of fatigue stresses is very much more damaging than the combination of non-oxygen exposure and fatigue stresses.

Fatigue tests by Haigh and Jones²⁴ in both atmospheric exposure and exposure in a bath of oil, gave the result that at a given stress the cycles required to fracture were more than two to four times greater in the case of the specimens in oil than those tested in air. It was then found that tests made with specimens immersed in distilled water likewise gave greatly improved behavior over those in air. The authors attribute fatigue-cracking

* Elastic limit—200 lbs. per sq. in.; tensile strength 1800 to 2500 lbs. per sq. in.

failure to the penetration of oxygen, the effect of the baths of distilled water and oil being to slow down the rate at which oxygen is supplied at the metal surface. Tests made in acetic acid immersion failed to produce cracking, the authors attributing this result to the complete prevention of oxygen access beyond the corrosion reaction layer.

Hardening lead with alloying elements allows a much higher range of stress fatigue, as compared with soft lead, before the damaging embrittlement condition is attained. Thus ⁵ the fatigue limits, in Table 87, obtained with alternating stress in the Haigh machine in ordinary atmospheric exposure, may be considered direct indications of resistance to intercrystalline embrittlement. The metal in all cases was annealed 1 hour at 482° F.

TABLE 87.—*Lead in Fatigue.*

Alloy Composition %		Fatigue Limit Lbs. per sq. in.
99.9	Lead	450
3	Tin	1080
1	Antimony	1390
.3	Cadmium	940
.5	Cadmium	1320
.25	Cadmium, 1.5 Tin.....	1140
.25	Cadmium, .5 Antimony.....	1590
.05	Tellurium	1140 ⁴⁷

TWO-METAL GALVANIC CORROSION

Available indications of the two-metal galvanic behavior of lead are few. As already stated, lead is more like iron than copper is in its tendency to displace hydrogen from aqueous solution. This similarity to iron holds roughly in respect to the galvanic behavior of lead. There is a certain vagueness about the relationships between lead and other metals in couple that seems to be due to the fact that the protective coatings on lead suppress and upset the relationships that might exist in the absence of coatings. One such case is that of a Monel metal tank whose welded seams were filled with lead. After two-months use in handling dilute sulfuric acid, the lead in the portion of the vertical seam above the solution level had almost entirely disappeared, whereas the lead beneath the solution level was apparently sound and the Monel metal sheet in the zone adjacent to the seam had suffered definite accelerated attack. As with most reported examples of galvanic attack, it was difficult to differentiate in this case between ordinary general attack, localized solution-cell attack, and two-metal galvanic attack. It seemed likely at the time that galvanic action was partially responsible, with Monel cathodic above the solution level and anodic below. It is common practice to use lead seams in Monel metal equipment for handling sulfuric acid, and the results are usually satisfactory.

Evans¹⁷ has obtained some interesting results on lead:iron couples in sodium chloride and in carbonate tap water. The electrodes of a couple were held 2.2 cm. apart, partially immersed for 14 days. The steel specimens were of 2.5 cm. breadth, the lead both 2.5 and 5 cm. (See Table 88.)

TABLE 88.—*Lead: Iron Couples vs. Salt Water.*

	Corrosion Rate of Iron—Mg. per sq. dm. per day	
	Sodium Chloride 0.1 N	Tap Water
Coupled		
Lead breadth—2.5 cm.	33	13
Lead breadth—5 cm.	19	12
Uncoupled	27	12

Tests on Monel metal: soft solder couples in hot tap water²⁹ have shown that strongly accelerated corrosion of solder is possible when the area is small as compared with the area of a cathodic metal like Monel metal. In quiet exposure at 200° F., with solder .20 sq. dm. in area and Monel 30 sq. dm. in area, the rates in Table 89 were obtained.

TABLE 89.—*Solder: Monel Couple vs. Hot Water.*

	Corrosion Rate of Solder Mg. per sq. dm. per day
	2.2
Uncoupled	
Coupled	335

On the other hand a similar test in water at 150° F. failed to give any accelerated attack, the rate for coupled solder being 1 mg. per sq. dm. per day.

Two-metal galvanic couples of lead with copper alloys are relatively common in equipment handling sulfuric, phosphoric, and sometimes sulfurous acid. Ordinarily, where the corrosion product film on the lead is highly protective, as in sulfuric, the danger in couples of this nature is lessened. Corrosion if it does take place will be centered on the lead. One set of tests in a boiling dilute sulfuric-nitric mixture found antimony lead cathodic to active stainless steel and anodic to passive stainless steel. The accelerated corrosion of the anode in each case was moderately intense, the electrodes being of equal area. The solution was moderately corrosive to uncoupled lead and strongly corrosive to active stainless.²⁹

ACIDS

Lead equipment is commonly used in the concentration and handling of sulfuric and phosphoric acids, in handling the sulfite solutions of the paper mill digester, in plants for sulfonation and chlorination, and with hydrofluoric under some conditions, and chromic. Against acetic, hydrochloric, nitric, and other acids lead has not a good degree of resistance and is seldom used. The results in Table 90²⁵ give a good comparison of the

behavior of lead in quiet nitric, hydrochloric and sulfuric acids at room temperature. The protective effect of the lead sulfate coating kept the attack of sulfuric low. The rates with hydrochloric are rather high, from the commercial standpoint, and those for nitric very high. Agitation-aeration would have been accelerating with all three acids.

TABLE 90.—*Lead vs. Acids.*

Acid	Mg. per sq. dm. per day	
	4 Hours	28 Days
Nitric1.2%	2200	230
Hydrochloric7%	360	25
Sulfuric 1%	<60	<1

Whitman and Russell's tests ⁵⁴ give a comparison in agitated solutions. The extremely corrosive nature of nitric and acetic acids is well illustrated. Concentrated nitric is shown to be much less corrosive than dilute; lead is sometimes used in handling greater concentrations than 70%, in which the hydrogen-ion concentration is relatively low. The attack of sulfuric is again seen to be low, relative to the other acids, with little variation in rates from 6 through 20 to 50% solutions. The action of sulfuric in these tests was inclined to be greater than usual because of agitation, and perhaps because the full protection of the sulfate coating was not felt over the 5-hour period. The tests were run at 68° F. over a 5-hour period, with oxygen and hydrogen gas respectively bubbling through the solutions. (See Table 91.)

TABLE 91.—*Lead vs. Acids.*

Acid	Mg. per sq. dm. per day	
	Oxygen	Hydrogen
Sulfuric		
6%	79	79
20	118	47
50	134	95
93	355	292
Hydrochloric		
4%	1280	134
20	8700	870
Nitric		
30%	68,500	64,600
70	1360	768
Acetic		
6%	8200	2130
glacial	50,000	4560

The effect of agitation-aeration as an accelerant of attack of hydrochloric and nitric is given by the data in Table 92.⁸⁸ The acids were 5 normal in concentration, and the tests were run for 5 hours at room temperature.

TABLE 92.—*Lead vs. Acids.*

	Mg. per sq. dm. per day	
	Quiet	Motion
Hydrochloric	36-180	10,000-20,000
Nitric	5,500-11,000	270,000-420,000

The results in Table 93²¹ on two acids—hydrochloric and acetic—that are considered too corrosive to lead to make it useful in handling them,

TABLE 93.—*Lead vs. Acids.*

	Mg. per sq. dm. per day	
	Hydrochloric	Acetic
Total immersion		
Quiet	111	111
Air-agitated	330	730
Alternate immersion		
Continuous	840	13,500
Intermittent	360	4,430
Spray (30 days)	119	2,050

illustrate the extreme variability in attack introduced by agitation-aeration and alternate immersion. The tests were made with 1 normal solutions at room temperature, the duration being 48 hours following 48-hours previous exposure. It is interesting to note here that the acetate of lead has a much higher solubility in water than the chloride.

Another set of data³⁷ are given in Table 94 to illustrate also the aeration-agitation factor. The solution was cider vinegar standardized to 4.27 acetic acid. The tests were run at room temperature, for a 100-hour period.

TABLE 94.—*Lead vs. Acid.*

	Mg. per sq. dm. per day
Quiet immersion	77
Aerated	355
Spray	2130

Sulfuric Acid. The resistance of lead to sulfuric acid solutions^{26, 32, 33, 35} may be roughly summarized as follows:

1. Lead acquires a coating of lead sulfate that is very highly protective under a wide range of conditions. It is due entirely to this coating that lead can be used at all against sulfuric.
2. At ordinary temperatures lead can be safely used with concentrations up to 75 to 85%. Quiet conditions yield rates in the range <1 to 10 mg. per sq. dm. per day. Agitation-aeration conditions are accelerating, resulting in rather variable behavior; under maximum conditions rates may become as high as 100 to 300 mg. per sq. dm. per day.
3. Concentrations above 75 to 85% become increasingly though variably corrosive at room temperatures. Rates range from about 10 to perhaps 350 mg. per sq. dm. per day; the factors determining where in this range the rates will lie in any case are not recognizable.

4. Elevated temperatures have a moderate tendency to increase the rates of solutions in concentrations to 75 to 85%. Rates in warm and hot dilute and moderately high concentrations lie usually in the range of 1 to 200 mg. per sq. dm. per day, with maxima at perhaps 400 to 500 mg. per sq. dm. per day. Warm and hot concentrated acids become extremely corrosive, rates ranging from 500 to several thousand mg. per sq. dm. per day.
5. Lead is inclined to be relatively insensitive to the aeration factor in the dilute to moderately concentrated range of solution, where the sulfate coating is effectively protective.
6. Where the sulfate coating is effectively protective, impurities in lead have little influence on corrosion.

Huge quantities of lead go into the construction of sulfuric acid manufacturing equipment, particularly in the chamber process. In this the lead handles, with a high degree of success, acid ranging from 48° to 50° Bé (60 to 62%) to as high as 60° Bé (77%). Marshall ³⁶ believes that 61° Bé (79.43%) acid and its corresponding boiling point—approximately 400° F.—are the desirable joint maxima for useful behavior. The observations of Jones ³⁰ in Table 95 indicate the high degree of resistance of lead in actual service in chambers.

TABLE 95.—*Lead vs. Sulfuric Acid.*

Yrs. in Use	Chamber	Remarks
11	first	Corrosion along crystal boundaries.
11	second	Surface very much scored in form of irregular channels. Measurement at thickest point 0.136 in., at thinnest 0.079 in.
9	first	Very even and regular action, leaving even surface.
20	second	Pin-head size pitting, some of considerable depth.
14	first	Very even corroding; attack around crystal boundaries but does not leave crystals in relief.
16	second	Rough surface with tear-shaped depressions.
20	third	Very good condition, no defects.
5	first	Scored surface, deposit of sulfur and lead sulfate has aided resistance.
14	fifth	Very good condition, no defects.

In discussing the action on lead in the chamber process of sulfuric manufacture, Grosvenor ²² states:

"The corrosion going on continuously, though slowly, is augmented by higher temperature, excessive moisture in the gases, increased niter content, absence of SO₂, too rapid movement or impingement of the gases, or alternate action of liquid acid and gases. The points of most severe attack therefore are as follows: around the entrance to the first chamber, owing to the heat, richness and velocity of the whirl of gases circulating to join the incoming stream; the end opposite this entrance (if the first chamber is not very long) owing to richness and impingement of the entering stream; the whole of the first chamber because the tempera-

ture is higher, the gases richer and reaction more active; any points where the sides are uncooled by the outside air, as points in contact with timber framework, the inner sheet of a lap joint, the bottom when it rests on the floor if it is not covered with mud or a layer of liquid, and side curtains where they descend inside the bottom pan; the last chamber where all SO₂ is pretty well exhausted, acid mist is much thinner and where in the absence of SO₂ the reaction N₂O₄ + H₂SO₄ = NO₂HOSO₂ + HNO₃ takes place (or with excess moisture even the reaction (2NO₂ + H₂O + O₂) = 2HNO₃)."

Chemical lead is ordinarily used in this country for chamber plant construction, hard lead for some parts. Jones (England) ³⁰ is authority for the statement that antimony is regarded nowadays as a very injurious impurity, particularly against the higher concentrations and temperatures. In England a test that is believed to give an indication of the quality of the metal as a corrosion resistant in chamber construction consists of heating the specimen in concentrated sulfuric and observing the temperature at which bubbles first evolve and at which the lead suffers rapid decomposition. Jones states that suitable chemical lead evolves gas at 374° to 392° F. and decomposes at 572° to 594° F.; many hundreds of specimens of lead manufactured by the Parkes' process have given the data shown in Table 96.

TABLE 96.—Lead vs. Sulfuric Acid.

	Gas evolution	Lead decomposition
Min.	295° F.	363° F.
Max.	413° F.	536° F.
Ave.	368° F.	455° F.

Sulfuric with other acids. As will be shown later the presence of sulfuric in phosphoric acid is extremely favorable to the good resistance of lead. Mixtures of hydrochloric or nitric with sulfuric on the other hand go far towards destroying the resistance lead has to sulfuric alone. The effect is illustrated by the data in Table 97. The tests were made at 77° F., though other conditions were not described. Sodium chloride in sulfuric is likewise accelerating.¹¹ (See Table 98.)

TABLE 97.—Lead vs. Sulfuric Mixtures.

Acid Concentration—%			Mg. per sq. dm. per day
Sulfuric	Hydrochloric	Nitric	
20			10
18	2		320
15	5		1,790
10	10		4,890
5	15		8,560
2	18		13,000
18		2	24,000
15		5	very great
10		10	very great
5		15	very great
2		18	very great

TABLE 98.—*Lead vs. Sulfuric Mixtures.*

Acid		Temp. ° F.	Mg. per sq. dm. per day
Sulfuric %	Sodium Chloride %		
8.3	1.7	59	150
		104	180
		140	200
		176	210
		212	2,200
31	17	122	1,400
		167	3,300
		212	3,600
33.3	6.7	50	8
		59	64
		104	72
		140	64
		176	310
		212	1,400

Hydrochloric acid. Hydrochloric acid ^{26, 33} solutions are sufficiently corrosive to chemical lead that seldom may the two be used together with satisfaction. In very dilute acid (under 1%) when cold, unaerated and unagitated the action is on the order of 80 to 100 mg. per sq. dm. per day. This is not severely corrosive, but perhaps high as compared with rates on other corrosion-resisting material. The data ²¹ given on page 208 illustrate the effect of aeration-agitation.

In quiet 5 to 20% solutions at room temperature ³³ rates have run on the order of 150 to 200 mg. per sq. dm. per day.

Antimony in lead is extremely beneficial to its resistance to hydrochloric, up to fairly high concentrations of acid and at higher temperatures. Whitaker ⁵⁵ has stated that 10 to 25% antimonial lead stands up well in cold hydrochloric of any strength, and in concentrations below 18%, up to 212° F. Calcott and Whetzel ¹¹ give the data in Table 99, without a clear description of exposure conditions, and without stating the antimony content of the lead.

TABLE 99.—*Hard Lead vs. Hydrochloric Acid.*

Acid Conc.	Mg. per sq. dm. per day	
	68° F.	212° F.
1%	10	10
5	10	60
10	20	60
35	100	240

Nitric acid. Nitric acid as a rule cannot be used with lead. The exception is that highly concentrated solutions have only slow action on lead. A case has been cited of lead containers lasting several years holding strong

nitric. Veley⁵⁰ gives the solubility of lead nitrate in nitric acid, as shown in Table 100. This suggests that the very slow action of highly concentrated

TABLE 100.—*Solubility of Lead Nitrate.*

Conc. %	Parts of Lead Nitrate per 100 Parts Solution
0	64.91
15.76	10.25
22.76	5.98
29	3.01
40.31	1.61

acid is due to low solubility of the nitrate, much as concentrated sulfuric acid builds up protective iron sulfate on iron. Forty per cent nitric is extremely corrosive to lead—over 100,000 mg. per sq. dm. per day—yet 95% acid at 68° F. has in one case¹² given a rate of 380 mg. per sq. dm. per day. Unfortunately other data on high concentrations appear not to be available.

Acetic acid. Acetic solutions corrode lead freely, and lead is definitely unsuitable for handling them. Tests by Calcott and Whetzel¹¹ have given rates of 150 to 240 mg. per sq. dm. per day for solutions of 0.5 to 60% acetic, under quiet submersion conditions. The tests were at room temperature, and were run for 48 hours following previous 48 hours exposure. The data on page 208²¹ indicate the extremely strong effect of aeration-agitation.

Phosphoric acid. Lead is commonly used with the impure phosphoric acid solutions obtained from phosphate rock by leaching with sulfuric acid. The pure acid is moderately corrosive, as rates later on will indicate, whereas the impure acid, hot and cold, is extremely well resisted.

Quiet immersion for 250 hours in phosphoric at 60° F. led to rates as given in Table 101.⁴⁰

TABLE 101.—*Lead vs. Phosphoric Acid*

Conc.	Mg. per sq. dm. per day
Pure acid	
76%	450
42%	160
Impure acid	
42%	<1

The pure acid was made from combustion of phosphorus, whereas the impure acid was derived from superphosphate and carried sulfuric acid and other impurities. The presence of sulfuric was believed to be responsible for the good behavior. It was determined at the same time that a 7% antimony lead alloy did not have the good resistance of ordinary lead to the impure acid.

Other tests³¹ have likewise brought out the fact that hot impure phosphoric is resisted far better by lead than is hot pure acid. The solutions were at 176° F., and were aerated with the exception that in the concentrated crude acid the specimens were partially immersed in the quiet solution. (See Table 102.)

TABLE 102.—*Lead vs. Hot Phosphoric Acid.*

Conc.	Mg. per sq. dm. per day
Pure acid	
50%	580-1150
25	400-1420
10	35- 720
Crude acid	
dilute	1 to 7
conc.	2.1 to 2.3

Clarkson and Hetherington¹⁴ concluded from a series of tests that the resistance of lead favored its use for the construction of a saturator for making ammonium phosphate and for linings on storage tanks and tank cars handling phosphoric. The tests were made at ordinary temperature in 65, 72, 80% acid, and at 212° F. in a saturated solution of ammonium phosphate carrying 10% by volume of 72% phosphoric, without agitation. Phosphoric solutions in sugar house work are handled by lead and antimony lead pipes, fittings, tank linings, etc. Continuous circulation of phosphoric through lead pipe, in one case quoted,¹ in the presence of oxygen led to the dislodging of "the lead phosphate coating," causing corrosive and abrasive action.

Sulfurous acid. Lead is one of the few metals that can handle sulfurous acid solutions and moist atmospheres of sulfur dioxide. As in the case of sulfuric, a protective coating forms, presumably sulfite. As a result the resistance of lead is almost perfect. Lunak³⁴ has quoted a virtually zero corrosion rate for lead exposed in four different sulfite digestors, where the temperatures ran 275° to 295° F., the solution carried 3.6 to 4.4% free sulfur dioxide, and the pressure ran 125 to 146 lbs.

Lead and antimony lead are in common use in equipment handling acid sulfite solutions in the pulp mill.

Hydrofluoric acid. Lead is used to some extent against hydrofluoric acid in the cold. A rate of 900 mg. per sq. dm. per day has been obtained in quiet, 2-hour exposure at 176° F. in 48% acid.²⁹ This of course must be considered very rapid.

Chromic acid. Chromic acid solutions, such as chromium-plating baths, are handled very satisfactorily with lead. Lead chromate has extremely low solubility.

Impurities in Lead vs. Acid Resistance. Lead of different grades of purity differ somewhat in resistance to acids. A good study of this subject has been made by Burkhardt.⁸ He found that of a large number of specimens varying in impurities, those behaving the worst were corroded at rates 3 to 5 times those behaving the best. The tests were made in sulfuric and hydrochloric and covered conditions where rates were on the order of 1 to 10 to as high as several thousand mg. per sq. dm. per day. The purest grades of lead were among the better specimens, grades with impurities that are unevenly distributed, among the worse.

CAUSTIC ALKALINE SOLUTIONS

Lead is amphoteric and the plumbates resulting from reaction with alkalis are very soluble. As a result strong caustic solutions attack lead relatively rapidly. The action is not so rapid as that by acids like hydrochloric and acetic, yet is sufficiently greater than the action on steels, and certain other non-ferrous metals, that lead is considered of poor resistance. The set of data in Table 103²¹ gives perhaps the clearest story, bringing out

TABLE 103.—*Lead vs. Caustic Solution.*

	Mg. per sq. dm. per day
Total immersion	
Quiet	74
Air-agitated	370
Alternate immersion	
Continuous	5,500
Intermittent	2,200
Spray (30 days)	9.5

the accelerating influence of aeration and the particularly poor resistance under alternate immersion exposure. The tests were made in one normal sodium hydroxide at room temperature, and ran for 2 days following a previous 2-day exposure.

Other tests^{11, 25, 52} confirm the very corrosive action of caustic solutions on lead.

AQUEOUS AMMONIA

Ammonium hydroxide is very much weaker than caustic alkalis in its effect on lead, though the action is definite enough compared with action on iron. The data in Table 104 in a one normal ammonia solution are well illustrative.²¹ The tests ran 48 hours following previous 48-hours exposure. The tests were made at room temperature.

TABLE 104.—*Lead vs. Aqueous Ammonia.*

	Mg. per sq. dm. per day
Total immersion	
Quiet	15
Air-agitated	9
Alternate immersion	
Continuous	29
Intermittent	25
Spray (30 days)	3

NEUTRAL SOLUTIONS

Corrosion product solubility and structure play the most important role in determining resistance of lead to the neutral range of aqueous solution. Rates of attack range from high, where the product is poorly protective, to negligible where the product is continuous and adherent. Under the best protective conditions, typified by the films forming in atmospheric exposure, the rates range around 1 mg. per sq. dm. per day and less. Where poorly protective, typified by the alkaline solutions characteristic of unset cement, rates range around 40 to 50 mg. per sq. dm. per day.^{6, 7}

Lead carbonate and probably oxide are the usual corrosion product under neutral aqueous conditions. The oxide in itself is not particularly protective, as shown by the fact that distilled water, aerated in the absence of carbon dioxide, is moderately corrosive to lead. Tap water as a rule is considerably less corrosive, though varying with the salt and gas contents. Silicate even in small quantities⁹ suppresses corrosion very markedly. As little as 0.06 gram of silicate ion per liter will prevent corrosion of lead by distilled water, and it is likely that even lower concentrations will have a suppressive effect.* Lime, chromate, sulfate, carbonate, bicarbonate are likewise suppressive. With substances of this nature rates probably invariably keep well below 1 mg. per sq. dm. per day. Chlorides have less beneficial effect, though undoubtedly are suppressive as compared with distilled water. Nitrates, due perhaps to the high solubility of lead nitrate, are inclined to be more damaging than chlorides. The presence of small amounts of nitrates in soil waters increases the corrosive attack on lead decidedly.* Waters carrying organic acids like acetic become rather strongly corrosive, although of course acid sulfate waters and salts are well resisted. Moderately to strongly alkaline waters are rather actively corrosive.

The data in Table 105²¹ compare two types of salt solutions, a more corrosive salt, sodium chloride, and a less corrosive salt, dichromate. The tests were made at room temperature and were run for 48 hours following previous 48-hours exposure.

* R. M. Burns, private comment.

TABLE 105.—*Lead vs. Salt Solutions.*

	Mg. per sq. dm. per day Sodium Chloride-1 N	Potassium Dichromate-1 N
Total immersion		
Quiet	32	6
Air-agitated	40	4
Alternate immersion		
Continuous	45	3.2
Intermittent	24	4.5
Spray (30 days)	3	<1

An interesting set of data has been reported¹⁸ on corrosion of lead submerged in quiet salt solutions over a 200 day period, at 46° F. (See Table 106.)

TABLE 106.—*Lead vs. Salt Solutions.*

Salt	Conc. Grams/liter	Mg. per sq. dm. per day
Water (no salt)46-.60
Sodium chloride	2.5-60	1.8-9.7
Potassium chloride	2.5-15	3.4-7.0
	40-80	.69-.80
Potassium nitrate	5-100	7.4-24
Sodium sulfate	2.5-20	.24-.72
	50-200	.021-.039
Potassium sulfate	2.5-80	.11-.80

In another set of tests⁴⁵ lead plates were immersed in solutions for 14 months, with the results given in Table 107. The concentration of salts was not noted:

TABLE 107.—*Lead vs. Salt Solutions.*

	Mg. per sq. dm. per day
Calcium carbonate	2
Calcium bicarbonate	1.3
Sodium carbonate	5.2
Magnesium sulfate	2.2

Lead is used to some extent in sea water, and generally gives satisfactory results. An indication of behavior is afforded by the results of tests¹⁹ in which lead bars were exposed in Bristol (England) Channel for 4 years, at a location where they were submerged 93% of the time. Corrosion rates for both soft lead and 1.6% antimony lead were on the order of 2 mg. per sq. dm. per day; localized attack did not take place.

Lead pipe¹⁵ has for many years been used in large quantity for conducting fresh waters. The life of lead in this service is virtually unlimited except in very rare cases. Recently lead pipe in good condition was uncovered in Rome that was believed to have handled water far back in the first century A. D.¹⁶

The question of whether lead is suitable or not for handling waters centers around the toxicity of the lead dissolved by the waters when subsequently ingested, rather than on durability considerations. Lead in its toxic effect is considered cumulative.⁵³

As a general rule hard waters absorb much less lead than soft waters. In fact it is usually considered perfectly safe to use lead with hard waters and for the most part necessary to avoid its use with soft waters. Presumably protection by the lead carbonate-lead oxide corrosion product that develops in hard water is the reason for its lesser corrosiveness. Waters characterized by temporary hardness likewise are considered safe to handle with lead. The presence of carbon dioxide in soft waters is believed to be particularly undesirable, in that greater pickup is favored. Silicates have been used by the English to prevent lead poisoning by very soft waters.*

Quantitative data throwing some light on lead pickup and the corrosiveness of waters have been developed by a number of investigators.^{13, 43, 45, 53} Weston's results⁵³ bring out a number of interesting points: (1) varying corrosiveness of different waters, (2) decreasing rate of attack in some cases, (3) accelerating effect of aeration, (4) suppressing effect of lime and magnesia. Lead sheet specimens (10.1 sq. cm.) were exposed for one day to waters held in open test tubes, the volume of water in each case being 10 cc. (See Table 108.)

TABLE 108.—*Lead vs. Waters.*

	Lead Pickup p. p. m.
Distilled water	182
Boston tap water (soft)	65
Poland Spring water	44
Poland Spring water charged	90
Vichy water	10
Distilled water with peat extract	6
Boston tap water with peat extract	2

Lead pipe specimens placed in sealed bottles under conditions uniform for all samples, led in 6 days to the following pickup as shown in Table 109.

TABLE 109.—*Lead vs. Waters.*

	Lead Pickup p. p. m.
Metropolitan water	129.
Milford water	9.5
Aerated	54.5
15 p. p. m. chalk added	14
15 p. p. m. chalk added and aerated	17
Aerated, with 8.5 p. p. m. quicklime added	22.5
8.5 p. p. m. quicklime	1.1
12 p. p. m. lime, then aerated	1.4
20 p. p. m. lime, then aerated	1.4

* R. M. Burns, private comment.

These results of course are of comparative value, one with another, only.

Weston also gives the analyses in Table 110 of Milford, Mass., water, to indicate the effect of lime treatment:

TABLE 110.—*Lead vs. Waters.*

Year	Parts per million			
	Average Lime Added	Hardness	Free Carbon Dioxide	Average Lead Pickup
1914	0	13	18.6	.27
1915	12.9	30	.30	.124
1916	12.1	24	.25	.10
1917	11.4	34.9	.40	.09
1918	11.1	31.8	.23	.082
1919	10.0	36.7	1.40	.085

Average analyses of corrosive and non-corrosive ground water, with lead pickup from pipe, are given in Table 111.¹³ Forty or fifty waters sampled throughout Massachusetts are included. The standing samples were taken from water that had stood several hours in the pipe.

TABLE 111.—*Lead vs. Waters.*

	Lead—p. p. m.	
	Corrosive Water	Non-corrosive Water
Carbonic acid	29.3	13.3
Hardness	34	30
Dissolved oxygen	48% sat'd.	44% sat'd.
Lead		
Running sample65	.15
Standing sample	1.70	.40

The analyses in Table 112, average and maximum, were obtained on 70 samples of Boston Metropolitan surface water taken after considerable length of service pipe.

TABLE 112.—*Lead vs. Waters.*

	Lead Pickup p. p. m.
Carbon dioxide	3
Dissolved oxygen ..	95% sat'd.
Lead	
Running sample, ave.13
Standing sample, ave.19
Running sample, max.34
Standing sample, max.63

The lead pickup from lead strips exposed to waters of different Illinois towns held in stoppered bottles for two weeks are given in Table 113.⁴³

TABLE 113.—*Lead vs. Waters.*

	Parts per million					Mg. Lead Loss
	Hardness	Alkal.	Chloride	Residue	Lead Pickup	
Decatur	121	160	2	302	.11	59
Cedar Point	222	150	295	1009	.025	46
Stronghurst	1100	216	259	2971	.23	16
Danforth	156	290	530	1374	.2	89
Chenoa	240	304	550	1276	.5	66
Norma	110	542	1010	2743	.43	26
Mt. Sterling	725	379	1310	4076	.2	31

Lead poisoning ⁴ has been a common enough occurrence among workers in lead industries—painting, printing, lead mining, smelting and refining, manufacture of storage batteries, pottery, enamel. Lead poisoning from waters drawn from lead pipes is rare, considering the widespread use of lead pipes. Back through the years poisoning seems to have been rather rampant due to the use of lead cooking utensils, and in other cases to the lead added to wine for fermentation purposes.

Authorities differ as to the quantities of lead ingested from waters, that will cause poisoning. This is not surprising in view of the different degrees in which different people are susceptible and the difficulty of establishing a quantitative relation between lead ingestion and poisoning. Hunt has made the compilation in Table 114 ⁵³ of lead contents in waters that have led to poisoning.

TABLE 114.—*Lead vs. Waters.*

Location	Lead p. p. m.
Westphalia5-1.6
Taunus7-12.5
Sheffield998-9.98
Huddersfield	1.99
Huddersfield	1.14-11.98
Manchester	1.4-4.28
Castle Claremont	2.0-15
Keighley	8.7

Weston has reported that in Dessau, Germany, water carrying approximately 4.14 p.p.m. lead caused many cases of poisoning, and that after the lead was reduced to 0.0 to 0.5 p.p.m. there were no cases in the subsequent ten years. After consideration of all available data on the subject Weston (1920) concluded that water with less than .1 p.p.m. lead would be considered safe, judged from practical standards. Howard ⁵³ in 1920 preferred .025 p.p.m., if lead in any quantity at all was to be allowed. The American Water Works Association ² considers .1 p.p.m. as the maximum for natural waters.

Very large tonnages of lead are used as sheathing for underground cables; the Bell Telephone System has approximately 90,000 miles of cable underground.⁹ The function of the lead sheathing is to protect the con-

ductors from corrosion. The most commonly used composition is lead with small quantities of antimony; the 3% tin alloy is used to some extent, and pure lead carrying a very small quantity of calcium is a rather recent development. Alloying is intended to give better strength, corrosion resistance being virtually unaffected one way or the other.

Ordinarily the sheathed cable is carried in conduits of various constructions. Corrosion of the sheathing when buried directly in the soil occurs sometimes from soft waters, sometimes from waters carrying calcium hydroxide leached from concrete ducts, sometimes from acetic acid vapors emanating from creosoted Douglas fir wood ducts, sometimes from stray currents; with the latter corrosion may be localized both at anodic points, and at cathodic areas where the solution turns alkaline and becomes corrosive. Probably the most frequent cause is concentration cell action,⁹ the cells being set up by variations in the soils or in underground waters or by the manner of distribution of soil particles against the metal surface.

The results of Burns and Salley¹⁰ on the effect of particle size, duration of exposure, moisture content, and oxygen content on corrosion by soils are significant. Corrosion rates for lead buried in white silica sand of different particle diameters are given in Table 115. The moisture content was 4.2 to 3.5%, the humidity of the air nearly 100%, the temperature 104° F., and an excess of oxygen was maintained in the atmosphere.

TABLE 115.—Lead vs. Moisture in Sand.

Particle size mm.	Mg. per sq. dm. per day	
	195 hrs.	3601 hrs.
2-1	67	12
.5-.25	54	11
below .05	38	4.2

The effect of moisture content as a variable in 30-day tests at 104° F. in white silica sand gave the data in Table 116.

TABLE 116.—Lead vs. Moisture in Sand.

Particle size mm.	Mean Moisture content %	Mg. per sq. dm. per day
2-1	0	3.8
	1.4	19
	5.5	20
	7.0	26
.5-.25	0	3.4
	1.9	19
	7	28
	11.2	22
below .05	0	2.1
	4.2	11
	10	24
	12.8	25

Further tests on varying oxygen in the atmosphere gave the results in Table 117. The moisture content was 4.4% and the tests ran 14 days at 104° F.

TABLE 117.—*Lead vs. Moisture in Sand.*

Particle size mm.	Atmosphere		Mg. per sq. dm. per day
	Oxygen	Nitrogen	
2-1	0	100	11
	1	99	23
	20.9	79.1	50
.5-.25	0	100	9.7
	1	99	22
	20.9	79.1	44
below .05	0	100	5
	1	99	13
	20.9	79.1	25

The same investigators compared the corrosiveness of several different soils. The moisture content was about 6%, except that it was 4.5% in silica, and the tests ran 2 weeks. (See Table 118.)

TABLE 118.—*Lead vs. Moisture in Earths.*

Particle size mm.	Soil	Mg. per sq. dm. per day
2-1	Sassafras gravelly loam	37
	Silica	50
.5-.25	Sassafras gravelly loam	27
	Silica	44
below .05	Sassafras gravelly loam	14
	Hagerstown silt loam	4.5
	Tidal moist	12
	Black alkali	8.2
	Silica	25

Stray electric currents as a source of corrosion of submerged pipe and sheathing is without a doubt a much less frequent occurrence than might be judged from the frequent references occurring in the literature. Solution-cells are powerful in their effect, and if the nature of the cells that are set up at the surface of buried lead could be determined it would very likely be evident that this type of cell is the cause of the greater part of the localized corrosion that occurs. Smith and Shipley⁴⁸ concluded, after extensive investigation of the corrosion of lead pipe in Winnipeg, Manitoba:

“Generally speaking, as much or more pipe corrosion has occurred in negative or neutral than in positive districts, irrespective of whether underground cables were near or distant.”

ATMOSPHERE

Lead has good general resistance to the atmosphere; the wide use of lead sheathing on aerial cable and of lead and Terne-plate as roofing,

cornicing, and spouting materials is a witness. In Table 119 are given corrosion rates (weight loss rates) covering a year's exposure in various atmospheres.²⁸

TABLE 119—*Lead vs. Atmosphere.*

	Mg. per sq. dm. per day
Rural44
Suburban61
Mild industrial59
Urban	1.15
Marine55

Lead exposed on a roof-top in Birmingham (England) was corroded as shown in Table 120²⁰ over a 7-year period. This represents extremely

TABLE 120.—*Lead vs. Atmosphere.*

	Mg. per sq. dm. per day
Pure lead29
Lead with 1.6% antimony04

good behavior compared with other materials.

Development of protective corrosion product layers is the reason behind this resistance, as in the case of resistance of lead to acids, salt solutions, and waters. The film is probably oxide.⁵¹ Its development is accompanied by rapid dulling of freshly abraded metal.

The nature of the film that develops and the degree in which it becomes protective, depend on atmospheric conditions at first exposure. This is clearly illustrated by the curves given in Figure 25.⁵¹ Curve A represents

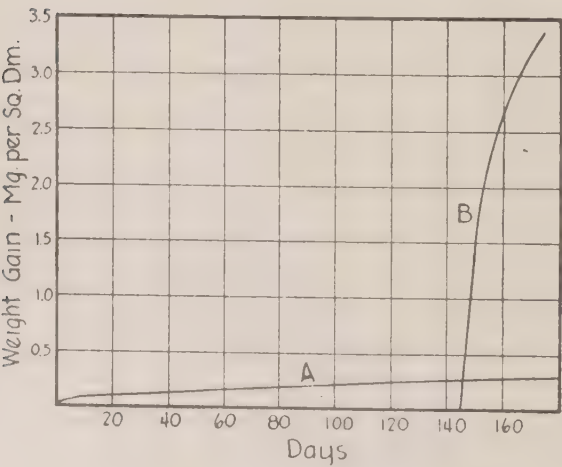


FIGURE 25. Lead vs. Basement Atmosphere.

the weight increment for lead exposed in a basement atmosphere. After 140 days fresh specimens were exposed and the rate of increase in weight (Curve B) was found to be quite different from the first; it was believed that the effect was due to the presence of turpentine in the atmosphere, derived from nearby drying paint. Curve A was not affected by this since the protective film had already developed. It is interesting to note that the rate of weight increment in Curve A grows continually less even after 160 days.

From the practical standpoint, therefore, the resistance of lead to the atmosphere is very good. Occasional occurrences of unsatisfactory behavior have been traced to unusual conditions. In one case cast lead sheets became perforated in places where in contact with oak beams but remained sound where resting on pine wood-work. Long experience has shown that contact with oak will lead to rather rapid attack.^{6, 7}

CONTACT WITH CONCRETE

Fresh concrete, according to Burns * is markedly corrosive to lead but the practice of precasting and aging the concrete, during which process the lime in the concrete surfaces becomes carbonated, results in a less corrosive conduit. In this case, however, water seeping through the conduit may leach out calcium hydroxide and cause corrosion. When lead is corroded by alkali (whether it be calcium hydroxide or caustic soda which is sometimes produced by electrolysis of sodium chloride solutions in contact with the surface of the sheath) the attack is characterized by the appearance of a reddish corrosion product which upon analysis will be found to be the red crystalline form of lead monoxide. This product is easily distinguished from the brownish to black lead peroxide which sometimes is formed as a result of anodic stray current attack.

HIGH TEMPERATURES

Lead and high lead alloys are not of use in high temperature work, since the melting points are low, and strength low at temperatures above the boiling point of water. Unreinforced lead with heavy walls may handle up to 50 lbs. per sq. in. steam pressure.** Pilling and Bedworth³⁹ found that lead oxidizes comparatively rapidly at 572 F°. to a reddish-brown oxide that is smooth and tightly adherent. Throughout a 7-day test quadratic proportionality between weight increment and time was observed, showing the protective nature of the oxide.

* R. M. Burns, private comment.

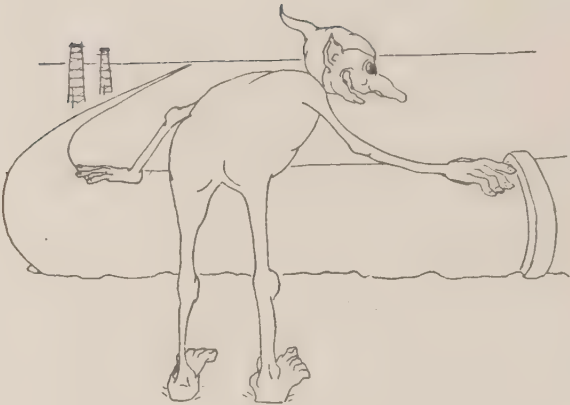
** G. O. Hiers, private comment.

LEAD

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Chapter XI

Iron and Steel

Iron and steel would fill practically all the metal construction requirements of industry were it not for chemical instability. The cost-per-pound of commercial ferrous metal, thanks to quantity production, availability of ore, and a remarkably efficient metallurgical science, is roughly one-third the cost of lead and zinc, one-fifth that of copper, one-tenth or less that of aluminum, nickel and tin. Furthermore, the physical properties of iron are generally desirable and the mechanical properties singularly versatile. Prevention of corrosion by metallic and non-metallic coatings and by the development of iron alloys has taken long strides towards filling in where iron itself is deficient; still no corrosion-resistant substitute of equal cheapness has been as yet found.

Carbon steel, cast iron, and wrought iron are the most important types of the ferrous group; these differ from one another in mechanical properties and, broadly speaking, in applications. Steel is the high-strength form of ferrous metal, cast iron a cheap though relatively brittle form for complicated shapes and heavy sections, and wrought iron is particularly suitable for welding, machining and working qualities and toughness. Steels alloyed for high strength and toughness by the use of elements with power to give corrosion resistance, such as copper, nickel, chromium and molybdenum, are beginning to be recognized as valuable also for certain specific corrosion resistances.

In corrosion resistance these variations of iron and steels are roughly similar, and as a group quite distinct from non-ferrous metals. They rust in atmospheric and natural-water exposure, are rapidly attacked by most acid solutions, and deteriorate at high temperatures. Alloys of high iron content are produced that will resist each of these conditions. They contain substantial percentages of other metals, which makes them different in other ways and therefore these are treated in other chapters. A 14 to 16% silicon iron is remarkably good for acid conditions; alloys with 12 to 30% chromium

are good for some acids, for neutral solutions and for high temperatures; a high combined nickel and chromium content gives a series of iron alloys of very good resistance and mechanical properties; the nickel-iron series are unusual for certain physical properties; and a cast iron with 25% nickel, copper, and chromium is generally resistant.

CORROSION RESISTANCE.

GENERAL

The action of the atmosphere and waters on iron accounts in large part for the reputation iron has as a poorly resistant metal. It is true that these are the most commonly met conditions, yet it is equally true that iron is an unusually versatile resistant when the range of corrosive substances is viewed as a whole. In certain acid solutions, in alkaline solutions, against various gases and molten metals, iron is often the best available metal even when its advantage in cost comparisons is disregarded.

Iron corrodes in aqueous solutions, like other metals, by change from the metal to the metal ion. The acids ordinarily corrode iron strongly with hydrogen evolution; in this respect, generally speaking, iron differs from the more noble metals like copper, and the less noble metals which develop protective layers of corrosion product, like aluminum. Alkalies have only slight corrosive action on iron, due to the development of a protective corrosion product film; in this iron differs from aluminum, which corrodes rapidly, and copper and lead, which develop films of less protective nature. In the neutral range of aqueous solutions in the presence of air, iron has poor resistance, the film that develops being poorly protective at best.

AQUEOUS CONDITIONS

Regarded from the standpoint of factors controlling corrosion and rate of reaction on iron, aqueous solutions are of three types—acid, neutral, and alkaline—as indicated in Figure 26.¹³³

Within the acid range, the reaction involves hydrogen evolution of important magnitude and goes on essentially without the development of obstructive and protective films of corrosion product; the controlling factors are total acidity and hydrogen-ion concentration, with aeration accelerating in minor degree. Within the neutral range, hydrogen evolution though operative is repressed in rate by the facts both of lowered total acidity and hydrogen-ion concentration and of solid films of corrosion product. Corrosion rates within this range are determined by diffusion of oxygen through these films, and are largely independent of hydrogen-ion concentration. Finally, within the alkaline range corrosion product films develop in much more effective degree than in the neutral, resistance increasing with alkalinity

and hydroxyl ion concentration and being largely insensitive to the effect of aeration that is so marked in neutral solutions.

Approximation of Test Results

	Mg. per sq. dm. per day
Acid solutions	
Strongly acidic.....	10,000
Weakly acidic.....	100
Special conditions.....	10
Neutral solutions	
Aeration, agitation very high.....	above 30
Aeration high.....	10-30
Aeration low.....	1-10
No oxygen available.....	0-1
Alkaline solutions.....	under 1

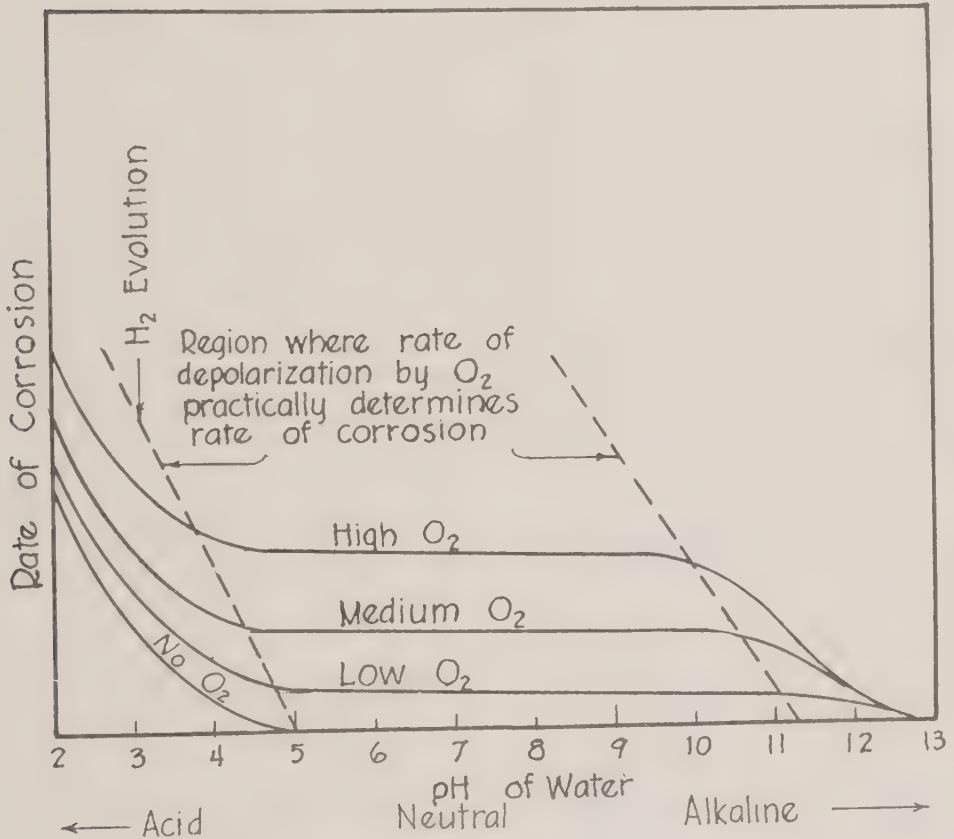


FIGURE 26. Iron vs. Aqueous Solutions.

The attack of acid and alkaline solutions normally goes on without important pits, whereas pitting is usual in neutral solutions. For neutral conditions therefore penetration rates range higher than represented by the average weight loss rates given above.

Neutral Solutions

Mechanism. Corrosion of iron by pure water begins at breaks in the invisible layer of oxide that normally exists on the surface of the metal.^{19, 40, 41} Reaction between the solution and the metal at these breaks leads to the withdrawal, from the diffusion layer against the metal, of hydrogen ions and dissolved oxygen, and the simultaneous introduction of ferrous ions into the diffusion layer. The layer of solution becomes concentrated in ferrous ions and reaction between dissolved oxygen and the ferrous hydroxide leads to precipitation of hydrous ferric oxide, which with ferrous hydroxide is recognized as rust.

Associated with these layers of hydroxide and oxide is the diffusion layer of solution that, in combination with the deposits themselves, obstructs the movement of reactants in the corrosion process and so controls corrosion rates. The influence of the diffusion layer of solution as an obstruction to the corrosion process is lessened as the thickness of the layer for any reason is lessened. The protective effect of the solid film likewise varies, depending on how closely adherent and how nearly continuous it may be.⁹⁴

Two important factors that affect corrosion rates by determining the properties of these liquid and solid layers are supply of dissolved oxygen and deposition of compounds other than the oxides of iron.

In the absence of air corrosion takes place and ferrous hydroxide is formed, but there is no subsequent formation of ferric hydroxide. Corrosion rates are low because hydrogen evolution is suppressed by cathode polarization. With the presence of moderate amounts of dissolved oxygen corrosion rates are increased because diffusing oxygen prevents cathode polarization. Variation in the dissolved oxygen content leads to variations in the physical characteristics of the precipitated ferric hydroxide films. Practically always, an increase in oxygen supply leads to greater corrosion rates.

Increase in the velocity of the solution, both by supplying oxygen at a greater rate and by thinning the diffusion film, generally leads to an increase in corrosion rates. Higher velocity, however, promotes greater protectiveness of the ferric hydroxide film, and as a result corrosion rates at times decrease with increasing velocity.⁹⁵

Relative acidity or alkalinity within the neutral range, as already pointed out, is a minor factor as an influence on corrosion rates. It is true that in the absence of air the rate of corrosion of the hydrogen evolution type varies with the hydrogen ion concentration.⁹¹ But this is as a rule not usually important practically, since corrosion of this nature is very slow, particularly when the metal surfaces carry salts like calcium carbonate precipitated from the solution. It is important, on the other hand,

in some cases; in the case of the tin can, for instance, failures known as "springers" are due to hydrogen evolution from corrosion.

The presence of dissolved salts in the water modifies the simple corrosion process just described, the salts taking part in reactions, both at the cathode and the anode, even though the end product continue to be ferrous hydroxide and hydrous ferric oxide. These salts influence corrosion rates by their effect on the adherence, location and physical nature of the rust layer and in the case of many salts by yielding a precipitate that adds to the obstructive effect of the rust and the diffusion layer of solution.

The two most important variables of iron corrosion under neutral aqueous conditions are therefore (1.) supply of dissolved oxygen, and (2.) deposited protective films. Average corrosion rates of iron submerged in quiet water, free of salts that may deposit out, yet containing dissolved air, range around 10 to 30 mg. per sq. dm. per day. Conditions like agitation or mechanical aeration are accelerating, and the deposition of compounds is usually suppressing.

Ferrous metals normally pit in neutral aqueous exposure. The reason for this is that the protection afforded by rust is ordinarily irregular. Breaks in the rust layers lead to greater rates of oxygen diffusion at some points than at others, with the result that oxygen solution-cells are promoted. A fact of importance here is that rust itself is a conductor and may act as a cathode in the corrosion reaction. The features of pitting under iron rust are too complicated to warrant extended discussion here *; it is sufficient to call attention to the susceptibility of iron and steel to pitting and to the fact that weight loss determinations do not fully take pitting depth into account.

Air-free Solutions. It has been said above that in the absence of air, corrosion of the hydrogen evolution type is usually slight to the point of being unimportant practically. Hydrogen evolution in waters both with and without air has been recognized up to a pH of 9.8.¹¹⁰ In these tests the water was at 180° F. and the rate of corrosion of the hydrogen evolution type was as high as 4 mg. per sq. dm. per day. Accumulations of hydrogen gas have been found in dead ends of hot water heating systems, and Speller¹¹⁰ believes hydrogen evolution accounts for the attack taking place in the absence of oxygen in deep wells and in certain soils.

Figure 27¹⁰⁹ gives a relation between pH value and volume of hydrogen evolved in the absence of air. Corrosion rates of about 13 mg. per sq. dm. per day, the corrosion taking place by hydrogen evolution, were observed¹⁴ in tests in which steel specimens were submerged in salt solutions carrying air. In the absence of air no hydrogen evolution was detected at the end

* Baylis¹³ particularly has studied this phase of corrosion of iron water pipes. Evans³⁷ also has considered the question.

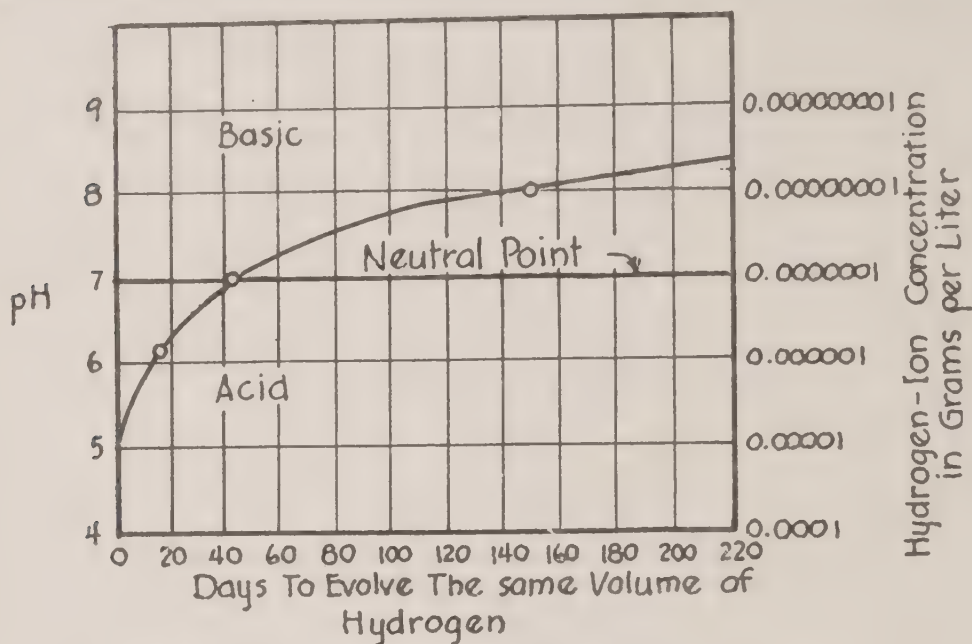


FIGURE 27. Iron vs. Aqueous Solutions in the Absence of Oxygen.

of 110 days. Submersion of steel and cast iron in salt solutions which previously had been boiled to remove dissolved air and from which air was excluded during test^{56, 57} led to rates of 4 to 15 mg. per sq. dm. per day. The attack was presumably of the hydrogen-evolution type, though detection of hydrogen was not attempted.

Tests in citric acid of .5% concentration and in solutions of this acid buffered with sodium citrate, covering a pH range of 2.41 to 5.54 gave rates of (at least) 40 to 8 mg. per sq. dm. per day, in the absence of air. The corrosion became progressively less as the pH value increased.⁹¹ The results indicated that with even a slightly lower pH value than 2.41 the rate of hydrogen evolution would become greatly accelerated. These tests were of 4-day duration. It is shown in Figure 34 that hydrogen evolution becomes rapid at about this pH value in hydrochloric acid.

Variation of attack with constituents in solution. Attack by neutral solutions varies somewhat with the constituents of the solutions, as already stated, through alterations in the nature of the diffusion layers against the metal. Evans³⁵ has studied the effect of salts that take part in the actual corrosion reaction at either anode or cathode, and has concluded as follows:

"The corrosion of iron and steel by a drop of aqueous liquid depends in most cases on electrochemical action between the central, unaerated area, which becomes anodic and suffers attack, and the peripheral aerated portions, which become cathodic, and in general remain unattacked. The velocity of attack depends largely on whether the anodic and cathodic products are soluble or

insoluble. In the case of pure water, the anodic product, ferrous hydroxide, is perceptibly soluble, and spreading outwards becomes oxidized at the junction between the aerated and unaerated regions, yielding a brown ring of the nearly insoluble ferric hydroxide, which extends over the top of the drop as a membrane. The action of salts (in *N/10* concentration) may be classified as follows:

(1) Salts like potassium chloride, potassium sulfate and potassium nitrate yield a soluble anodic product (ferrous chloride, sulfate, or nitrate) and a soluble cathodic product (potassium hydroxide), and increase the velocity of corrosion; where the ferrous salt and alkali mingle, a ring of ferrous hydroxide, oxidizing to ferric hydroxide appears, and extends as a membrane over the surface. Outside the membrane the iron is unattacked, but the formation of alkali at the periphery (cathodic portion) causes spreading of the liquid.

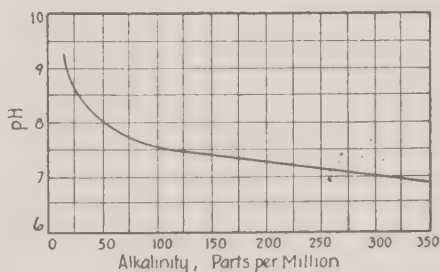
(2) Salts like zinc sulfate yield a soluble anodic product, but an insoluble cathodic product (zinc hydroxide), which shields the cathodic area from diffusing oxygen, slightly diminishing the rate of corrosion.

(3) Salts like sodium carbonate, sodium phosphate, and potassium ferri-cyanide yield a soluble cathodic product and an insoluble anodic product, which forms a closely adherent protective skin, usually invisible, over the metal. In such cases, corrosion is almost prevented; but occasionally at certain points, especially at the edge of the drop, the film fails to adhere, and at such points marked localized anodic corrosion occurs; the breakdown occurs quite quickly in more dilute solutions of sodium carbonate.

(4) Potassium chromate causes passivity even in those parts to which oxygen cannot diffuse; no differential-aeration currents are set up, and there is practically no corrosion. If, however, chlorides also are present in large quantity, the protective film breaks down at the edge, and serious localized corrosion will result; nitrates act more slowly than chlorides in causing the breakdown of the film, whilst sulfates are still less active in this respect."

Water supplies relatively high in calcium carbonate are less corrosive by several times than those without this salt. Baylis¹² has constructed the curve as given in Figure 28 to indicate the boundary in calcium carbonate alkalinity where its protection is felt.

FIGURE 28. Approximate Solubility
Equilibrium of Calcium Carbonate.



Treatment of water supplies deficient in calcium carbonate with sodium carbonate or sodium hydroxide brings about the desired alkalinity—pH relationship. Free carbon dioxide tends to prevent the deposition of carbonate or to dissolve it. Lime deposits in boilers are protective, the allowable oxygen in the water being higher where these are present. Waters which carry too little carbonate to deposit on the boiler walls are sometimes treated with lime.

Silicates likewise depress corrosion rates of iron, important in some water supply systems carrying silicate, and likewise as a treatment method for municipal water supplies. In laundry water supplies 15 parts per million of silicate is a common dose.

Other substances improving resistance are zinc sulfate, sodium carbonate, sodium phosphate, potassium ferricyanide, chromates.^{47, 68} Refrigerating brines are commonly treated with sodium chromate or with a mixture of sodium dichromate and sodium hydroxide. These brines—concentrated solutions of sodium chloride, calcium chloride, or a mixture of calcium and magnesium chlorides—have each a concentration range where the corrosive effect is least and the attempt is made to keep the brine within this range. It is common practice to prevent aeration as much as possible and to keep the brines on the alkaline side. Whitman and co-workers¹²⁸ found a chromate content of 0.17% in brine to depress attack by as much as 90%.

Danger from pitting lies in the careless use of inhibitors.³⁶

In steam systems carbon dioxide gas is undesirable from the fact that it tends to acidify the steam condensate and thereby increase attack of iron. The same effect is felt with waters high in magnesium chloride, which hydrolyzes at higher temperatures to an acid reaction. These waters lie at the neutral-acid border line. (See Figure 26.) Trouble from either carbon dioxide or magnesium chloride can be eliminated by proper treatment.

Salts hydrolyzing acid in aqueous solution—aluminum chloride and sulfate, and soluble salts of tin, copper, mercury and ferric iron—are corrosive. Protective films are not formed in these and the free acid corrodes with hydrogen evolution. Acid mine waters are of this nature.

Strongly alkaline salts such as sodium carbonate and sodium silicate on the other hand act like alkalis and are well resisted by iron.

Comparison of types of ferrous metals. Some variation in resistance to neutral conditions exists among the different types of ferrous metals—cast iron, wrought iron, steel, copper bearing steel, etc.—but with few exceptions the variations are not predictable in degree or kind nor are they important from the commercial angle. Variations are likely to show up in tests of relatively short duration and do most definitely show up in atmospheric exposure tests even of long duration. These two conditions have in common a capacity for forming a relatively thin film of corrosion product, in this respect differing from long-time-submerged exposure and the resulting characteristically thick film. Chappell²¹ found the rust-film thickness on sheet irons and copper steels after atmospheric exposure to be about .0005 cm., although the irons were badly corroded and the copper steels were in relatively good condition. He records a rust layer thickness of .15 cm. from submerged exposure. He has further shown by using films of filter paper that corrosion rates are progressively lower as the thickness of

the film increases. The thicknesses studied covered the range of rust-film thicknesses of both atmospheric and submerged exposure. Experience has shown that in atmospheres copper steels (0.20 to 0.25% copper) may be several times more resistant than steels without copper, yet in submerged exposure over a long period of time no significant difference appears.

After weighing the available evidence of differences in resistance among the different types of ferrous metals, Speller ¹¹⁰ has stated "with respect to wrought iron and steel in general, the great preponderance of evidence points unmistakably to the conclusion that there is no inherent difference between these materials with respect to durability."

Evans ³⁸ has considered the comparative resistance of wrought iron plate that had been rolled in two directions and steel and has concluded that under conditions giving intense localized corrosion wrought iron (so manufactured) is likely to have better behavior because pits tend to spread out rather than to penetrate deeply as in the case of steel. "In general, it may be said that under favorable conditions there is no reason why steel should not have a life similar to that of wrought iron, but that the peculiar structure of wrought iron gives it, under certain circumstances a definite advantage in deflecting an attack of an intense localized character." It is important to note that by rolling in two directions the cinders in wrought iron are worked out into plates. Wire and pipe are not so processed and therefore the conclusions of Evans do not apply to them.

Cast iron and steel are likely to differ in behavior against neutral solutions. Girard ⁵⁶ for instance found that in dilute aerated sodium chloride solution, cast iron corroded evenly with the development of a continuous protective rust film, whereas steel suffered localized and continuous corrosion under a poorly protective layer of rust. The difference was very marked over a period of several months. He furthermore found that in the relative absence of air the behavior of the two was much alike, without in either case the development of a layer of rust. The corrosion rates, based on weight loss, were as given in Table 121.

TABLE 121.—*Iron vs. Sodium Chloride Solutions*

	Corrosion rate—mg. per sq. dm. per day	
	Aerated	Not aerated
Steel	10.6*	11.0
Cast iron ³	8.1-7.6	9.5-11.7

* Strong localized attack.

Friend ¹⁰² likewise found cast iron less susceptible to localized action, in sea water (see page 238).

Deaeration. Since corrosion of iron is so largely dependent on dissolved oxygen, deaeration is a common preventive method. The solubility of oxygen in relatively pure water ranges from about 10 cc. oxygen per liter

at 32° F. to about 0 cc. at 210° F.¹¹⁰ Soluble salts decrease the oxygen solubility. Fresh waters are usually air-saturated and according to Speller 95% of dissolved gases may be removed fairly easily by means of deaerators. In these, water is subjected to temperature and pressure combinations suitable for extraction of the dissolved gases. They are in common use, of one type or another, in industrial water and steam systems. In recirculating systems, such as in household steam and hot water heating, deaeration is not usually required since dissolved oxygen originally present is used up in a relatively short time and is not sufficient in quantity to cause notable corrosion damage. Very little corrosion may be expected over as much as a 70-year period.¹¹⁰ It is particularly desirable in systems of this nature to prevent air leakage. Corrosion conditions on steam locomotives are much more severe than in stationary plants since the water, originally air saturated as a rule, is not deaerated.

Deactivation.¹¹⁰ Another means of removing oxygen from water is by pre-corrosion. The fresh water is run over a large area of replaceable iron plates held in a tank. In a properly designed deactivator, attack of these plates removes most of the dissolved oxygen, in some cases all of it.

Sea water. Corrosion of iron and steel by sea water still remains an undefeated problem. Where possible, of course, protective coatings such as galvanizing and paints are applied. Steel and cast iron construction of ships is an example. Protective coatings are not long-lived, requiring continual repainting. Metal so cared for, however, will last for many years.

Sea water is characteristically both air-saturated and a very good electrolyte; both conditions promote corrosion. The fact that it is a good electrolyte favors localized action of the concentration cell and particularly the galvanic types. Inherently, air-saturated sea water is no more corrosive than air-saturated fresh water,¹⁰² but the currents of galvanic and concentration cells can flow through greater distances in sea water and therefore the cathodic area of a cell may become relatively large, and the corrosion more intense.

Many corrosion investigations have been made on iron and steel in sea water.^{14, 15, 33, 50, 51, 57, 75, 102, 103} Behavior has been particularly well outlined in an English investigation.¹⁰² Bars were exposed at four widely varying localities both below low water level and at half-tide level for periods of five and ten years. A summary of the results is given in Table 122. The weight loss results give average corrosion rates, including loss due to both general corrosion and pitting.

A number of interesting conclusions may be reached from a study of these results and the author's observations:

1. Effect of location. Corrosion at Colombo was only slightly greater than that at Plymouth in the five-year test. Corrosion at Halifax was 1.2 to 2

TABLE 122.—*Iron vs. Sea Water.*

	Halifax—10 yrs.			Aukland—10 yrs.			Plymouth—5 yrs.			Colombo—5 yrs.		
	Mg. per sq. dm. per day (Wt. loss)	In. per yr. (Max. penet.)		Mg. per sq. dm. per day (Wt. loss)	In. per yr. (Max. penet.)		Mg. per sq. dm. per day (Wt. loss)	In. per yr. (Max. penet.)		Mg. per sq. dm. per day (Wt. loss)	In. per yr. (Max. penet.)	
<i>Submerged</i>												
Irons—cleaned	26.6-29.6	.0030-.0078		12.5-13.4	.0026-.0069		17-23	.006-.015		16-20	.01-.04	
Steels—cleaned	22.6-24	.0042-.011		18-21.5	.0027-.0040		22-28	.003-.011		24-30	.006-.009	
not cleaned	21.3-25	.0019-.0074		14.8-17	.0077-.013		18-20	.012-.025		22-26	.018-.048	
Copper-steel—not cleaned	21-24.5	.0022-.0082		16-17	.0083-.011		19	.008-.022		18-22	.021-.027	
Nickel-steel (3.75 Ni)												
Not cleaned	17.7	.0064		12.1	.017		16	.025		16	.035	
Cast iron	17.3-20			14-16	.0021		7-8			24	.009-.022	
<i>Alternating Wet and Dry</i>												
Irons	8.9-12.2	.0010-.003		6.9-8.5	0-.0021		18-22	.006-.009		34-38	.014-.016	
Steels—cleaned	7.2-8.5	.0022-.0026		8.0-8.3	0-.0011		24-25	.008-.009		42-70	.006-.016	
not cleaned	8.7-16.5	.0011-.0037		3.3-5.7	0-.0029		13-16	.008-.02		38-70	.018-.04	
Copper-steels—not cleaned	7.9-9.5	.0022-.0025		3.7-3.8	.0016-.0017		12-16	.015-.014		46-52	.034-.042	
Nickel-steel (3.75 Ni)												
Not cleaned	3.7	.0027		3.0	.0043		11	.012		36	.024(perf.)	
Cast iron	2.0-2.1	.0071		1.5-2.2			6-9			54		

times greater than that at Auckland. Both at Colombo and Auckland the specimens became heavily coated with marine life, whereas those at Plymouth and Halifax were substantially free of life. If the presence of marine life has an effect on the total corrosion of iron and steel, this effect in these tests was obscured by other variables.

2. Effect of metal composition. So far as these tests indicate, there is nothing to choose between wrought iron, carbon steels, and steels carrying low copper or nickel. Specimens without mill-scale in general lost slightly more in weight than those with mill-scale, but were pitted to a slightly less extent. Cast iron definitely suffered less from pitting and general corrosion, but suffered an internal attack, possibly graphitization, that was as penetrating and damaging as combined pitting and general attack were to the other materials.
3. Effect of time. Five-year tests compared with ten-year tests, at Auckland and Halifax, indicate that average corrosion rates, both on the basis of weight loss and pitting, are somewhat less over the ten-year period.
4. Effect of exposure. At Halifax and Auckland, and to a less degree Plymouth, submerged exposure was more corrosive than half-tide exposure. At Colombo, curiously, half-tide exposure was 2 to 3 times as corrosive.

Boiler corrosion. Boiler corrosion^{3, 31, 60, 63, 89, 110, 116} is a special case of corrosion in neutral aqueous conditions. Water exposed freely to the air has normally on the order of 6 cu. cm. per liter of oxygen. If carried into the closed system of which the boiler is a part, all this oxygen would be available for the corrosion reaction, and attack would be very extensive indeed. As a preventive, oxygen in so far as feasible is removed by means of preheaters, deaerators, or deactivators. According to Speller* the oxygen must be reduced to 1 to .03 cu. cm. per liter to keep its damaging effect down. Some waters—those of higher acidity and those that do not deposit a thin protective type of film on the metal—require more extensive removal of oxygen than others.

Free and half-bound carbon dioxide, which has some corrosive power in the closed system, is also largely driven off by preheating.

Deaeration by itself is often not a sufficient preventive of corrosion. Some waters are acid and others carry salts, as magnesium chloride, that decompose under heat to form acid. Since acid will corrode iron seriously even in the absence of oxygen, it is necessary to treat such waters with alkali. It has been found that a minimum pH of 11 within the boiler is desirable, but that too strong an alkaline condition may lead to excessive pitting or to embrittlement attack (see later on).

Substances like calcium and magnesium carbonate, calcium sulfate, and calcium and magnesium silicate decrease in solubility with temperature rise. Treatment of feed water is common to prevent the excessive formation of a hard adherent scale of these substances within the boiler. These scales are undesirable not only because they cause overheating and poor heat transfer, but also because they promote localized conditions of high temperature and breakdown of acid-forming salts that lead to corrosion.

* Private comment.

Locomotive boilers are likely to have a more difficult corrosive condition than stationary boilers, due to the fact that the bulk and inconvenience of deaerating and pre-treatment equipment prevent taking full advantage of these.^{18, 59, 77, 110}

Certain special features of corrosion of steel boilers have been extensively studied within the last few years and the understanding of the mechanism of attack that has resulted has been an important contribution to corrosion data. The stresses to which boiler plate is subject are generally of a fatigue nature resulting from the vibration set up in the generation and release of pressure within the boiler. In the construction of a boiler it seems to be usual to allow a theoretical factor of safety of $3\frac{1}{2}$ to 5.¹¹³ The actual working stresses run probably considerably higher than the theoretical, due to such factors as poor alignment of rivet holes, stress concentration at the discontinuity of the holes, heat expansion stresses, stresses set up in the riveting, forced alignment.² It is believed that working stresses in some cases actually run up around the yield point. When stresses of this intensity are accompanied by certain corrosion conditions within the boiler, serious accelerated attack of one of two types takes place—deep transcrystalline pitting of the type associated with corrosion fatigue, or weakening penetration along grain boundaries.

Corrosion fatigue of boiler plate has been discussed by several.^{32, 85, 127} The important single factor bringing about this type of action is high cyclic stress; no association with any particular water condition seems to have been made although laboratory tests indicate that brackish and salt water and certain hard or alkaline waters are more damaging than fresh water, and fresh water more damaging than steam vapor. On the other hand corrosion fatigue cracks have occurred even with distilled make-up water. McAdam's laboratory investigations of corrosion fatigue have shown that exposure to simple aerated water when accompanied by cyclic stress of moderate intensity is extremely damaging to the strength of steel. The degree of damage is more dependent on the number of cycles of stress and on frequent wide variations of stress than on the time of exposure.

The principal weapon against corrosion fatigue of boilers is to keep working stresses down to a minimum. Dinger³² suggests that for ordinary Class "B" boiler plate the fiber stress should not exceed 10,000 lbs. per sq. in., and that 9,000 lbs. per sq. in. would be better. He believes that a factor of safety of six will give a safe boiler, of five a somewhat doubtful one, of four a dangerous and unsafe one.

The second serious type of boiler corrosion—intercrystalline weakening—occurs almost entirely at riveted seams.^{25, 113, 127} Cracks develop running along the line of rivet holes, at tube ends or at random along any seam. Instances of this nature are confined to three types of water:—(1)

natural alkaline; (2) waters made alkaline with soda ash treatment; (3) waters made alkaline by zeolite treatment.

The action differs from that of corrosion fatigue in that the change in the metal takes place in the intercrystalline material rather than in the crystal grains. Failures of this nature have been associated entirely, as far as known, with boiler waters of relatively high caustic soda concentration in combination with relatively low sodium sulfate concentration. The sodium carbonate in boiler water characteristically decomposes within the water to give free sodium hydroxide.^{73, 81, 114} Straub believes from the indications of laboratory tests, that caustic becomes concentrated in the capillary spaces of seams and tube ends and it is this condition combined with the high stresses in the metal that leads in some way to deterioration of the intercrystalline material. It is known that caustic attacks iron with liberation of hydrogen,¹⁶ and it also has been demonstrated¹³² that atomic hydrogen may lead to intercrystalline embrittlement.

Among Straub's laboratory results¹¹³ is the important one that in the case of ordinary steel, the susceptibility to intercrystalline penetration has been very marked at stresses just above the yield point under conditions where no effect was noticeable at a stress slightly under the yield point. His explanation seems a reasonable one—the stretching of the metal at and above the yield point breaks what protective layer of corrosion product may exist on the surface of the metal, thus facilitating further action and penetration of the damaging substance, whatever it may be.

Fortunately, means of preventing this type of failure are available. According to Straub, no case of failure has been experienced where the ratio of sodium sulfate to sodium hydroxide in the boiler water is above a certain minimum, the minimum depending on the boiler pressure. In the American Society of Mechanical Engineers Boiler Construction Code¹ it is recommended that the sodium sulfate should be maintained at the minimum values in Table 123 in relation to the sodium carbonate.

TABLE 123.—*Desirable Boiler Water Condition.*

Working Pressure of Boiler (lb. gage)	Relation of Sodium Carbonate Alkalinity to Sodium Sulfate
0-150	1 to 1
150-250	1 to 2
250 and over	1 to 3

The mechanism of the inhibitive effect of sodium sulfate is not entirely clear, but Straub's experiments suggest that it depends on concentration and precipitation of sulfate within the capillaries.

It is also known that in addition to sodium sulfate, other substances such as sodium carbonate (undissociated), tri-sodium phosphate, tannin, and other substances act as inhibitors to the damaging effect of the caustic,

so that a correct minimum ratio of sodium sulfate to sodium hydroxide should take into account possible concentrations of these other substances in the water. As preventive water treatment, sulfates, phosphates, tannin, sulfuric acid, etc. are added.⁹³ Straub¹¹³ recommends also the use of inside caulking rather than outside in order to prevent capillary accumulation of water. McCabe³ suggests a different approach—the elimination of riveted joints and their high internal stresses. Avoidance of the possibility of stresses around the yield point is, of course, a preventive.

Underground waters. Corrosion of buried pipe, though virtually nonexistent in many cases, becomes a serious problem with some soils. Attack when it does occur is of a highly localized nature, due to the action of solution-cells. In one case, 300 miles of pipe dug up after 35-years' service was in such condition that it was resold for use in other buried service. It has been figured that pipe lines may last as much as one hundred years in some localities. In extensive field tests⁸² irons and steels were corroded in underground exposure at rates ranging from .0002 to .005 inch per year (1.2 to 30 mg. per sq. dm. per day), based on weight loss determinations and were pitted at rates of .01 to .03 inch per year (60 to 175 mg. per sq. dm. per day). Potential differences of significant magnitude may exist in the ground,⁷⁹ and these undoubtedly have some influence on corrosion. More intensely corrosive cells, however, seem to be set up at the surface of the pipe due to irregular distribution of soil particles, and by variations in oxygen supply from point to point. The existence of "pipe line currents" has been demonstrated,⁷⁹ as well as the existence of earth potentials in the neighborhood of buried pipe. These are manifestations of cells that are often powerful enough to damage the pipes in a serious way. Kuhn⁸⁰ has found corroded spots on water mains to aggregate about 1% of the total exposed pipe area, with 8% as an extremely high value. The entire uncorroded surface of the pipe in such a case would be potentially cathodic. Fortunately, polarization, low rate of oxygen supply, and corrosion-product accumulation tend to suppress the flow of currents in these cells.

Water content of soil, air content, type of soil as this affects the mobility of the water, as it relates to the building of protective films (lime, etc.), and as it determines the specific corrosiveness of the soil, are all variable factors.

Stray currents where they exist, contribute to the corrosion of pipes by tending to intensify current density at anodic points and by influencing the polarity, magnitude, and distribution of both earth currents and "pipe line currents."

Buried pipe is ordinarily protected on its outer surface by paints, bituminous substances, fabric wrapping, etc., although of course these do not continue completely protective over long periods of time.

Food products. The main limitation in the use of iron for food handling equipment lies in its lack of resistance to the atmosphere and to aerated waters. Foodstuffs as a class carry high percentages of water and equipment handling them during processing has, as a rule, aqueous conditions in the neutral to acid range to contend with. Tin coatings and zinc coatings are protective methods, likewise glass enamel.

The presence of iron salts in foodstuffs is harmless from the standpoint of toxicity. The beneficial effect of iron taken into the human system is too well recognized to require comment.

Atmospheres. Irons and steels normally rust and pit in atmospheric exposure. The rate of attack is dependent on a number of variables, the most important being relative humidity, and impurities—dust particles, salinity, sulphur compounds—in the atmosphere. The film of moisture collecting on the metal in atmosphere of moderate to high humidity is air-saturated, and the corrosion products accumulating on irons and steels control by their physical character how corrosive this air-saturated solution will be. Dry atmospheres are not corrosive; thus, unprotected iron may last for centuries in dry climates without deterioration. In relatively pure atmospheres a critical humidity seems to exist, in the range of 43% to 68%, above which corrosion becomes marked.^{96, 122, 123, 124}

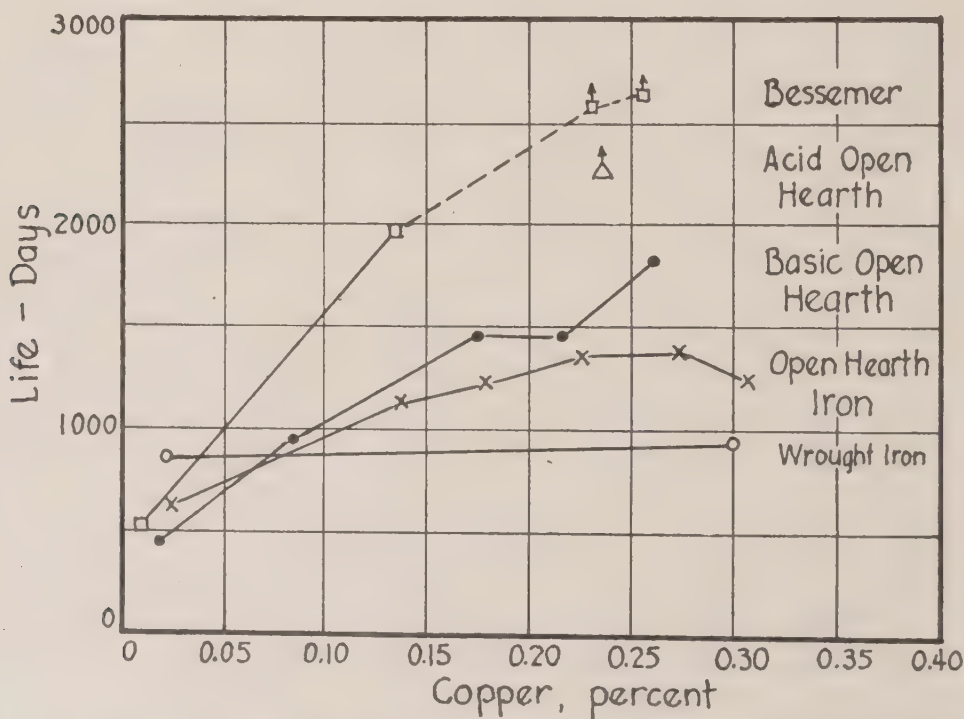


FIGURE 29. Iron and Steel vs. Industrial Atmosphere, Showing Effect of Copper Content. Specimens were 0.031 in. thick.

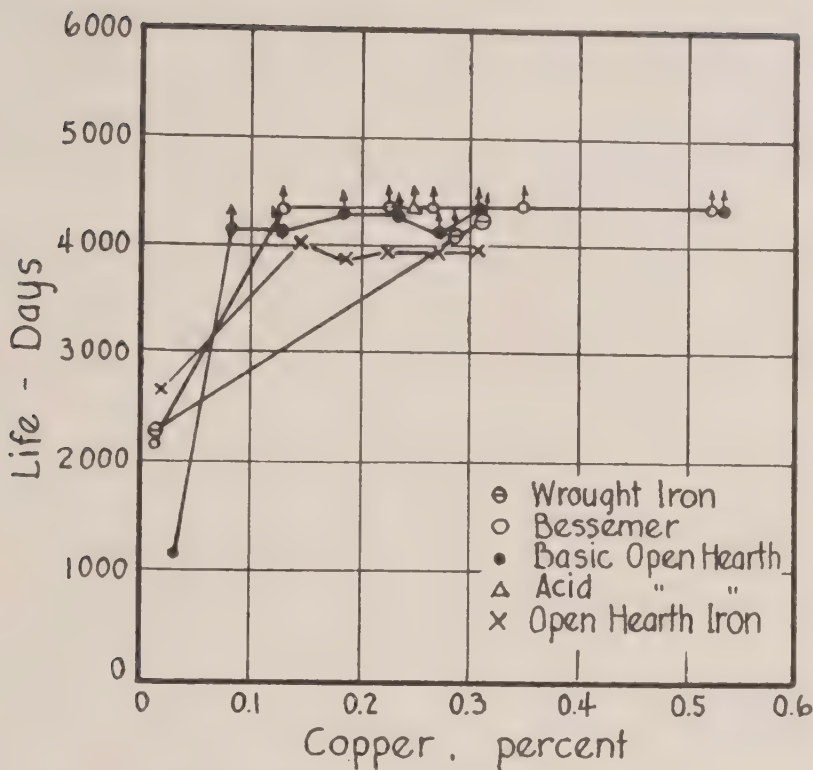


FIGURE 30. Iron and Steel vs. Rural Atmosphere, Showing Effect of Copper Content. Specimens were 0.031 in. thick.

Corrosion rates of ordinary iron and steel in atmospheric exposure are on the order of 6 to 40 mg. per sq. dm. per day, based on weight loss measurements for the more corrosive atmospheres, with pitting rates ranging higher than this—possibly 30 to 70 mg. per sq. dm. per day. Industrial atmospheres are more corrosive than marine or purer moist atmospheres.^{49, 104, 110, 129}

Steel and iron carrying a small copper content (0.15 to 0.25%) are more resistant by several times than ordinary steel and iron, the rust that forms being of a dense and hard nature, rather than loose and poorly adherent as characteristic of rust on ordinary iron and steel.^{11, 21} The effect is illustrated in Figures 29 and 30. The atmospheres were industrial (Pittsburgh) and rural (Fort Sheridan) respectively. The specimens were 22 gage (.031 inch thick).^{55, 74} Comparison of the two figures brings out the much more rapidly corrosive nature of the industrial atmosphere. Parallel tests have also been in progress in the seacoast atmosphere of Annapolis, Md. This proved to be less corrosive than the Fort Sheridan atmosphere, as shown in the table following.

Iron vs. Atmosphere.

	Annapolis	Fort Sheridan
Date begun	10/17/16	4/9/17
Date inspected ..	5/7/28	4/16/28
Number of sheets in test:		
Copper-bearing	148	136
Non-copper-bearing	79	83
Failures:		
Copper-bearing	1	50
Non-copper-bearing	23	77
Per cent failures:		
Copper-bearing	0.7	36.8
Non-copper-bearing	29.2	92.8

Copper-bearing steel and iron, like ordinary ferrous metal, require painting or other protection in atmospheric exposure. The advantage in the copper content, a very real one, lies in its better resistance at breakdown points in the protective coatings.

Iron and steel in most types of atmospheric exposure, even indoors, require protection to prevent rusting. With machine parts wiping with oiled rags is sufficient. Paints, metal coatings, and layers developed by controlled corrosion are other means, painting being the most useful. The principal deficiency of painting is its temporary nature, periodic painting being necessary for most purposes. Zinc (galvanizing) is the most common of the metal layers. Tin coating is common for small iron articles intended for mild exposure conditions. Tin and zinc coats are commonly painted. Cadmium plating is efficacious though expensive. Nickel and chromium plates, based largely on appearance requirements, are in wide-spread use. Aluminum, copper, and brass layers have minor use.

Neutral aqueous corrosion as revealed in fatigue tests: Stress accelerated corrosion. Probably the most sensitive instrument for measuring the damage suffered by metals in surface corrosion is the fatigue test. A great deal of investigation in this direction has, within the last few years, given extremely interesting results.^{58, 86} The more important conclusions relating to steels are given below, the term "damage" being used synonymously with "drop in fatigue limit."

1. Steels in an unstressed condition exposed to aerated water suffer damage of considerable magnitude, the rate of damage becoming less with time. Typical examples are given in Table 124; the water in this case was carbonate well water.
2. The application of alternating stress during the corrosion exposure period strongly intensifies the damage. The effect is shown by the curves below, in which factors of time, intensity of stress, number of cycles of alternating stress, and rate of cycles are related. In general, the rate of damage is greater with increase in each of these factors.
3. The application of alternating stress with corrosion exposure, destroys in time most of the advantage in strength gained by alloying and all the advantage gained by heat-treatment. Thus, a number of steels ranging in tensile strength from 52,000 to 260,000 lbs. per sq. in. had no apparent fatigue limit (1450 r.p.m., 30,000,000 cycles) range of 12,000 to 30,000 lbs. per sq. in. when exposed during the fatigue test to a stream

TABLE 124.—*Steel vs. Well Water.*

Days of stressless exposure prior to fatigue test	Resultant fatigue limit—lbs. per sq. in.		
	.46 C	.28 C 3.7 Ni	.39 C 1.82 Ni .92 Cr
0	43,000	65,000	75,000
2		53,000	64,000
4	41,000	48,000	56,000
10	37,500	44,000	48,000
50	34,000	37,000	45,000
100	37,500	35,000	
280	33,500		

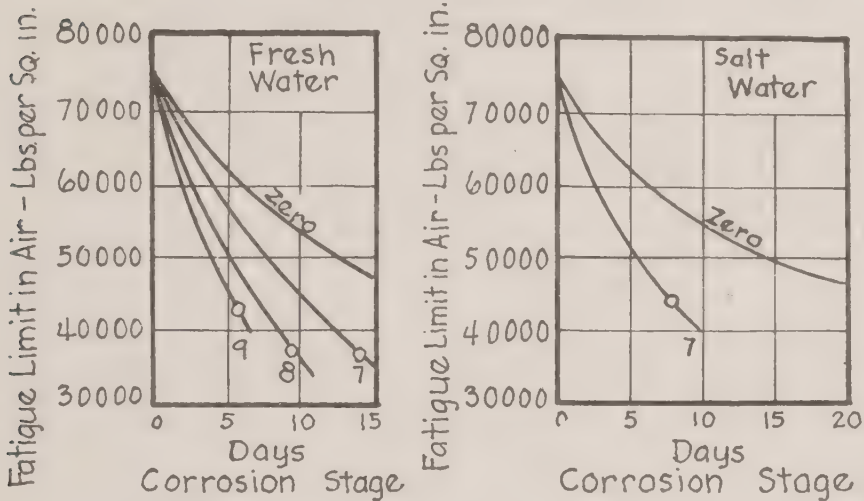


FIGURE 31. Chrome-nickel Alloy Steel vs. Fresh Water and Salt Water. The measure of damage is the drop in fatigue limit. The numbers on the curves refer to the stress (in thousands) applied during the prior corrosion exposure in the fatigue testing machine.

of carbonate well water. The alloy steels behaved slightly better than the carbon steels, and annealed steels slightly better than heat-treated. Nitrided steels seem to have remarkably good behavior under stress-corrosion conditions.^{52, 86}

4. Composition of the water has a large effect on the intensity of damage. Exposure of an unstressed alloy steel (.39C 1.82Ni .92Cr) in three different waters gave comparisons as shown in Table 125.

TABLE 125.—*Steel vs. Waters.*

Days of stressless exposure prior to fatigue test	Resultant fatigue limit—lbs. per sq. in.		
	Condenser Water	Carbonate Water	Brackish Water
0	75,000	75,000	75,000
2	72,500	64,000	64,000
4	70,000	56,000	56,000
10	65,000	48,000	48,000
20	61,500	45,000	44,500
40	59,000	45,000	43,000
60	58,000	45,000	42,000

Composition of the water is even more important where stress accompanies corrosion exposure. Thus, where the apparent corrosion fatigue limit (1450 r.p.m., 30,000,000

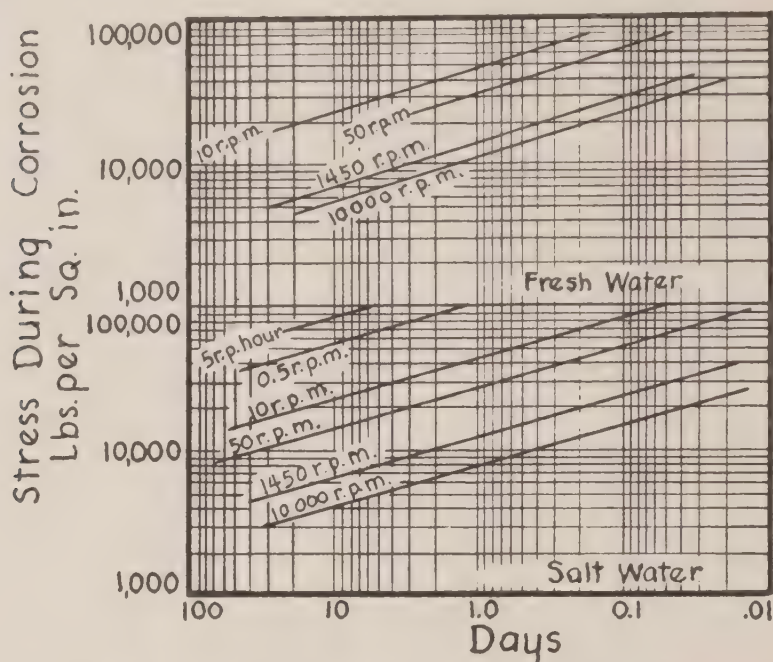


FIGURE 32. Chromium-nickel Alloy Steel vs. Fresh Water and Salt Water, Showing the Combinations of *Stress During Exposure, Time, and Rate of Rotation* of Specimens to Lower the Apparent Fatigue Limit by Fifteen Per Cent.

cycles) in carbonate water has, for various steels, averaged around 20,000 lbs. per sq. in., that in brackish water has averaged about 6,000 lbs. per sq. in. Steam is damaging, though to a less extent, than water.^{52, 69} Steam and air mixtures are much more damaging than steam in the absence of air.

5. Inhibitors in waters have been found to be very markedly beneficial.¹¹¹

6. Plated coatings of chromium and cadmium have been variable in their beneficial effect. McAdam⁸⁴ found cadmium to be very definitely beneficial, whereas Haven⁶⁶ could discover no advantage. With chromium, McAdam⁸⁴ found little if any benefit. Fuller⁵² found some benefit in one case, and Honneger⁶⁹ found definite benefit in one case.

Acid solutions.

With several important exceptions, to be noted later, acid solutions are mildly to strongly corrosive to iron and steel. The greater action of acids as compared with neutral solutions is due to three principal facts: (1) The invisible ferric oxide layer normally present on iron is rapidly destroyed by acids.⁴² (2) The hydrated oxides of iron, which are the secondary corrosion product of the reaction between iron and neutral solutions, are soluble in acids. (3) The hydrogen-ion concentrations of acid solutions make the latter inherently strongly corrosive to iron, even in the absence of oxygen (aeration).

It is generally true that higher concentrations of acids and of hydrogen-ion are more corrosive than lower; aeration, agitation, and tempera-

ture are accelerating. These factors influence the attack of iron much as they do the more noble metals like copper and nickel. An important difference, however, between iron and these other metals is that acids may be strongly corrosive to iron even in the absence of air, although aeration is accelerating.

Some acids are more corrosive to iron than others, as brought out by the data in the following pages, but this is practically not a very important point. Iron is too strongly attacked by almost all common acids of intermediate and dilute concentrations to make it a lasting handling material. Furthermore, with only few concentrated acids, e. g. nitric, sulphuric, chromic, can iron be used; these are mentioned again later. And with very dilute concentrations, iron is useful if the concentrations are weaker than about 1/1000 normality (pH 3 to pH 7). Even with these solutions, corrosion is mild to strong if the aeration conditions are severe.

Below are given typical rates of attack of iron by acids:

<i>Iron vs. Acids.</i>	
	Mg. per sq. dm. per day
Strongly acidic	10,000
Weakly acidic	100
Very concentrated	10
Special passivating conditions	10

An example of the low rates of attack in very weak solutions is given in the data below in simple immersion tests of 48-hours' duration in sulfuric acid ⁵⁶:

<i>Iron vs. Sulfuric Acid.</i>	
pH	Mg. per sq. dm. per day
7	7
5	5
4	7
3	9
2	70
1	540

Other acids as well as sulfuric are only weakly corrosive in similarly dilute solutions.

Typical corrosion rates in intermediate concentrations of low aeration degree (quiet partial immersion) are given in Table 126, these tests being run at room temperature for 5 days ⁷⁰:

TABLE 126.— <i>Iron vs. Acids.</i>		
Acid	Concentration	Mg. per sq. dm. per day
Hydrochloric	1%	195
Sulfuric	1%	174
Acetic	1%	230
Butyric	1%	142
Lactic	1%	144
Citric	0.2%	110

Aeration, as already stated, is accelerating. The rates in Table 127 were obtained in intermediate and high concentrations in 5-hour, room-temperature tests ¹³¹:

TABLE 127.—Iron vs. Acids.

Acid		Corrosion Rate—Mg. per sq. dm. per day	
		Hydrogen Saturated	Oxygen Saturated
Sulfuric	96.5 %	480	460
	50	1,100	1,500
	20	440	1,600
	6	180	2,100
Hydrochloric	4	180	2,800
	.04	32	2,300
Nitric	70	370	470
	1.2	9,000	11,000
Acetic	glacial	76	3,800
	6	37	3,200

An illustration of very strong acid attack is given by the data in Table 128 obtained in 24-hour tests with sulfuric acid at different temperatures ⁶⁵:

TABLE 128.—Iron vs. Sulfuric Acid.

° F	Mg. per sq. dm. per day		
	12%	38%	63%
59	14,000	20,000	200
104	40,000	82,000	600
140	45,000	125,000	1,000
176	50,000	127,000	1,100

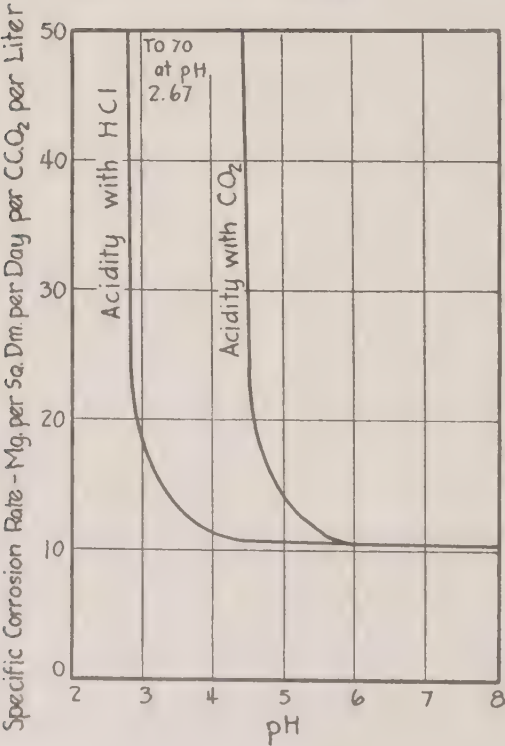
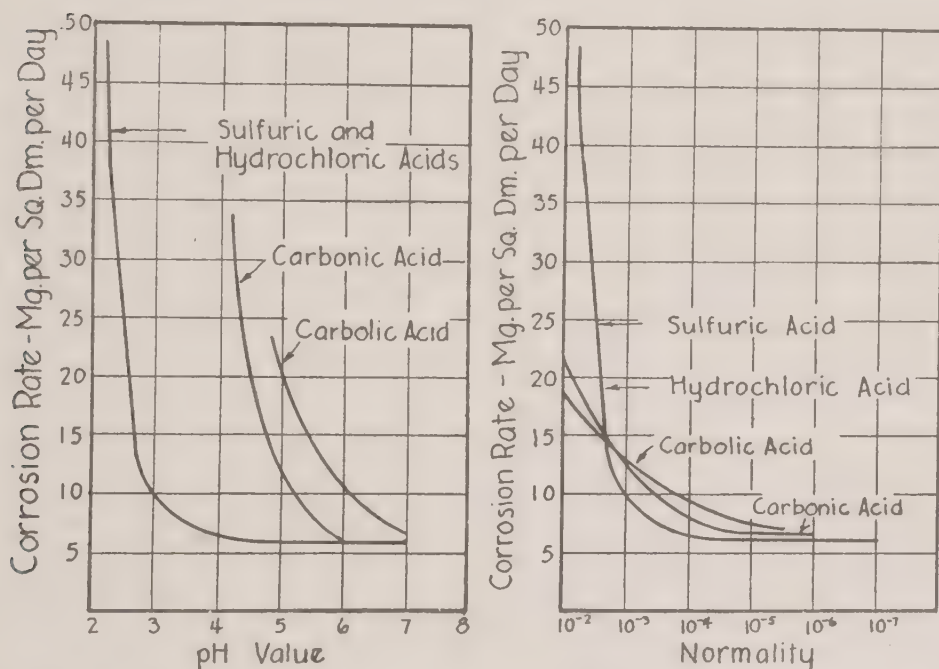


FIGURE 33. Iron vs. Aqueous Solutions, Indicating the Boundary Between Strongly Corrosive Acid Solutions and Weakly Corrosive Neutral Solutions.

Since neutral and very weakly acid solutions can often be handled with iron, it becomes important to note the boundary between these solutions and the more strongly corrosive acid concentrations. This division line is a rather indefinite one, depending as it does on aeration, acidity, and hydrogen-ion concentration as variables. The curves of Figure 33,¹³⁰ indicate that in moderately aerated hydrochloric acid the boundary exists at about pH 3, whereas in carbonic acid at about pH 4.5. These acids represent highly ionized and meagrely ionized types respectively.

Girard ⁵⁶ found a similar relationship between weakly and strongly ionized acids and found further, as given in Figures 34 and 35, that the boundary for both weakly and strongly ionized acids lay at about 1/1000 to 1/100 normality (e.g.—.0049 to .049% sulfuric acid). Thus, with increasing concentration, the different acids pass from the neutral to the corrosive acid zone at about the same normality, but at different concentrations of hydrogen-ion.



FIGURES 34 and 35. Iron vs. Aqueous Solutions, Indicating Increasing Attack with Increasing Acid.

On the other hand, acid solutions of intermediate concentration and higher, if of low aeration, are most corrosive when they have high hydrogen-

ion concentration. This relation is shown in Table 129, the criterion of attack being quantity of hydrogen evolved ⁸³ from specimens of equal area:

TABLE 129.—*Iron vs. Acids.*

Acid 0.20 N	pH	Duration (hrs.)	Hydrogen Evolved (cc.)
Hydrochloric81	18	25
Sulfuric98	18	25
Phosphoric	1.73	96	16.5
Tartaric	2.01	96	17.3
Malic	2.24	96	8.2
Acetic	2.57	96	2.5
Propionic	2.74	96	None

Yet aeration and agitation obscure the effect of hydrogen-ion as a factor and bring into prominence the effect of total acidity.¹³¹ (See Table 130.)

TABLE 130.—*Iron vs. Aerated Acid.*

		Mg. per sq. dm. per day	
		Hydrogen Saturated	Oxygen Saturated
Sulphuric 6%		180	2100
Acetic 6%		37	3200

Iron is commercially useful in handling strong concentrations of crude phosphoric acid (sometimes), nitric acid, and sulfuric acid, and in handling chromic acid. Chromic and nitric acids are strong oxidizing agents and thus maintain an insoluble and protective layer of ferric oxide on the surface of the metal.⁴² Since this layer tends to be dissolved off by the acid reaction and to be maintained by the oxidizing reaction, the oxidizing capacity of the solution must be dominant to produce passivity. In intermediate and dilute concentrations of nitric acid, the oxidizing reaction is overpowered by the acid, and the attack on iron is strong.

Chromic being a weakly ionized acid, and yet a strongly oxidizing one, is not usually corrosive to iron. Because of this passivity, iron is commonly used for the construction of tanks for holding chromium plating baths, where the solution runs in the neighborhood of 25% chromic acid. Friend ⁴⁸ has recorded that dilute chromic acid seems to have no action on cast iron over a one year period, and Evans ⁴² found that chromic acid did not dissolve flaky ferric oxide. He observed, however, that chromic acid in the presence of sufficient stronger acid (sulfuric) failed to produce passivity, but rather enhanced corrosion.

The good resistance of iron to concentrated sulfuric acid ⁴³ is fortunate since it makes possible the use of the various grades of iron in the construction of sulfuric acid plants, and the general handling, shipment and storage, piping, and valving of strong sulfuric with cast iron and steel equipment.

In the following tables are given several sets of data outlining the action of concentrated sulfuric acid. Wells and Fogg¹²⁵ have summarized as follows:

"Acids of all strengths from chamber acid to 100% H_2SO_4 have very little action on cast iron at ordinary temperatures. If boiling, the weaker acids attack cast iron vigorously. The action decreases as the strength of the acid increases until at 98% H_2SO_4 the iron is scarcely attacked at all."

They also state that acid below 100% acts more rapidly on wrought iron than on cast, especially at high temperatures. The data below do not show consistently better behavior for cast iron. The results in Table 131 were obtained in air-excluded sulfuric at 65° to 68° F. with a test period of 72 hours.⁷⁶

TABLE 131.—*Iron vs. Air-Free Sulfuric Acid.*

Sulfuric Acid %	Sulfur Trioxide %	Mg. per sq. dm. per day		
		Cast Iron	Ingot Iron	Wrought Iron
48.8	39.9	1600		
61.2	50.0	39		78
67.7	55.3	21		20
73.4	59.9	17		16
79.7	65.0	39		29
83.7	68.4	35		27
85.1	69.5	33		26
88.2	72.0	41		36
90.6	73.9	45		34
92.0	75.2	25		26
93.0	75.9	19	25	21
94.1	77.0	19	23	17
95.4	77.9	31	37	33
96.8	79.0	25	20	25
98.4	80.3	17	13	16
98.7	80.6	14	13	15
99.2	81.0	14	10	13
99.30	81.07	14	10	13
99.50	81.25	14	10	12
99.77	81.45	17	10	12
100.	81.63	22	23	19
	81.8	51	97	81
	82.02	48	72	113
	82.28	34	110	170
	82.54	39	240	270
	82.80	38	145	330
	83.50	20	190	390
	84.20	68	260	230
	84.62	69	350	190
	85.05	19	500	390
	86.00	18	62	120
	88.24	11	8	13
	90.07	10	5	5

The data in Table 132 were obtained at 65° to 70° F. in 50 to 65 hours exposure.⁹

TABLE 132.—*Iron vs. Sulfuric Acid.*

Sulphuric %	Mg. per sq. dm. per day	
	Cast Iron	Mild Steel
60	270	130
65	52	20
70	30	20
75	30	18
80	33	18
85	33	16
90	64	75
95	75	80
100	64	160

The data in Table 133 were obtained in 28-day, agitated tests at 86° F.:⁴⁴

TABLE 133.—*Iron vs. Sulfuric Acid.*

Sulfuric Acid ^d %	Mg. per sq. dm. per day
80	300
85	55
87.9	55
89.3	14
89.3	15
90	130
94	90
97.4	10

Concentrated sulfuric acid is moisture-absorbing and thus self-diluting. If left open to moist air, the acid will in time drop in concentration to as low as 35 to 40%, which is within the very corrosive range. This point is well to keep in mind.

Motion of concentrated sulfuric acid past an iron surface is sometimes an accelerating condition due, it is assumed, to removal of the protective coating of hydrous ferrous sulfate. The effect is illustrated by the data in Table 134 from 48 hour tests.¹³¹

TABLE 134.—*Iron vs. Sulfuric Acid.*

Acid concentration %	Mg. per sq. dm. per day		
	At rest	0.3 ft. per sec.	2 ft. per sec.
80.5	79		240
89	320		140
91.9	250		1100
94.8	100	170	430
97.8	120	1200	1000*
100.	1100	+	3800*

* Samples previously exposed at rest.

As the tests in 89 and 100% acid will indicate acceleration does not always result. The important point is that the possibility exists. Fawsitt and Powell⁴⁵ mention that agitation of acid in a drum by shaking or hammering the drum is sufficient to accelerate action noticeably.

A second characteristic of the action of concentrated sulfuric on iron is the slowing down of corrosion rates with time, important as a factor for consideration in applying corrosion rate data. Here again, the rule is not entirely inviolate, as indicated by the rate in Table 135 in 80.5% acid. The tests were made in acid at rest at room temperature.¹³¹

TABLE 135.—*Iron vs. Sulfuric Acid.*

Acid concentration %	Mg. per sq. dm. per day	
	First 48 hrs.	Second 48 hrs.
80.5	79	130
89.0	320	200
91.9	250	190
94.8	100	<6
97.8	120	63
100.	1100	<6

These results as well as those given before point to considerable variability in the action of concentrated sulfuric on ferrous metals.

Finally, Whitman and Russell¹³¹ found that steel specimens corroded at a very much greater rate at locations abraded by the glass rod by which they were kept in motion—a rate as high as 150,000 mg. per sq. dm. per day being obtained. The conclusion is reached that strong abrasion as well as agitation is sufficient to upset the protection of the sulfate film.

The action of fuming sulfuric acid is indicated by the data⁷⁶ on page 251. Although cast iron is attacked less from the weight loss standpoint, it is subject to an embrittling action when used with fuming sulfuric, due, it is believed, to reaction between sulfur trioxide of the acid and the silicon in the metal.^{7, 61}

The data in Table 136 were obtained in sulfuric-sulfur trioxide mixture at 65° to 72° F., in 50 to 60 hours exposure.⁹

TABLE 136.—*Iron vs. Sulfuric-Sulfur Trioxide.*

%	Mg. per sq. dm. per day	
	Cast Iron	Mild Steel
Free SO ₃		
24	50	80
20	18	80
15	30	220
10	42	260
5	50	200

In the pickling of iron and steels, usually accomplished in hot 2 to 15% sulfuric acid, it is desirable to prevent solution of the metal, yet at the same time to have the scale completely removed.^{4, 5} Certain organic substances added to the bath act as inhibitors to action on the metal, by forming

a film that obstructs the cathode (hydrogen evolution) reaction.²⁴ Proper use of inhibitors prevents "over pickling," pitting of the metal surface, hydrogen embrittlement, and excessive depletion of acid.^{4, 5, 10, 28} Chappell and Ely^{22, 23} tested the effect of a number of inhibitors, the better ones suppressing corrosion to 1 to 2% of that occurring in the absence of inhibitors. The tests were made in 4% sulfuric at 160° F.

Chapman²⁰ has given the data in Table 137 on steel in concentrated mixtures of nitric and sulfuric, presumably at room temperature.

TABLE 137.—*Sulfuric-Nitric Mixture.*

Mixed Acid		Mg. per sq. dm. per day
Sulfuric	53%	13
Nitric	45%	
Water	2%	
Sulfuric	74%	8.5
Nitric	9%	
Water	17%	

Bate⁹ found concentrated mixtures of nitric and sulfuric acids with up to 20% water were well resisted by cast iron and steel. With 25% water the attack was greater. His tests were made at 65° to 72° F., over a 50 to 65-hour period. (See Table 138.)

TABLE 138.—*Iron vs. Sulfuric-Nitric Mixture*

Concentration %			Mg. per sq. dm. per day	
Sulfuric	Nitric	Water	Cast Iron	Mild Steel
70	30		27	27
75	25		27	22
80	20		30	25
85	15		33	22
90	10		50	27
95	5		50	15
45	30	25	55	74
50	25	25	60	77
55	20	25	62	91
60	15	25	72	97
65	10	25	72	160
70	5	25	260	18,000

Nitric is extremely corrosive to iron and steel in dilute and intermediate concentrations. Five-hour tests with mild steel gave the data in Table 139.⁹⁰ Yet in concentrated acid, iron is in the passive state, with no appreciable corrosion.^{42, 90}

TABLE 139.—*Iron vs. Nitric Acid.*

Normality	Mg. per sq. dm. per day	Normality	Mg. per sq. dm. per day
1/10	1,630	2	112,000
1/5	4,200	5*	1,400,000
1/2	20,500	S.G. 1.42	120
1	53,000		

* 50 minute test.

According to Monypenny,⁹⁰ acid of 1.3 to 1.35 specific gravity (47 to 56%) at first attacks iron, then tends to become non-reactive. The common grade of concentrated acid is 65 to 70%. This lies within the substantially non-reactive range and is often shipped, mixed with concentrated sulfuric, in iron drums and tank cars. Thompson¹¹⁸ has reported corrosion rates of 10 to 100 mg. per sq. dm. per day for iron and steel in 68% acid. Yet Bate⁹ records very strong action of concentrated nitric carrying nitrous acid on cast iron. The tests were made at 65° to 70° F., and ran 50 to 60 hours. (See Table 140.)

TABLE 140.—*Iron vs. Nitric-Nitrous Mixture*

Concentration %		Mg. per sq. dm. per day	
Nitric	Nitrous	Cast Iron	Mild Steel
94	0.7	6,000	40
90	3.2	4,000	93
85	2.4	4,200	84
80	2.9	3,500	100
75	3.6	4,300	103
70	2.0	4,700	103
65	1.0	4,500	107

Crude concentrated phosphoric acid is well resisted by iron^{26, 90, 101} due presumably to the presence of some substance other than phosphoric. Arsenic has been inhibiting when added to pure phosphoric. Pure phosphoric, dilute and concentrated, is very corrosive to iron.

Is one type of ferrous metal better than another in handling acid solution? This point has been widely investigated; the only clear-cut generalizations resulting are that no one type of metal among the common unalloyed and low-alloyed irons and steels invariably is superior to the others, and that the apparent superiority of one type in any single set of conditions may not hold if the conditions are only slightly varied.

On page 251⁷⁶ are corrosion-rate data for three types of iron in sulfuric acid. The differences in apparent resistance are noticeable, yet it is very doubtful whether, in view of the vagaries of corrosion in general, these differences are at all reproducible or important. The data are given as an illustration of comparisons that are not widely useful, although the data as a whole are important.

By substantial additions of alloying elements to cast iron, resistance to acids may be greatly improved. Thus the silicon-iron alloys* are extremely good against acids. Another commercial alloy cast iron carrying 14% nickel, 6% copper, and 2 to 3% chromium is useful with acids. Throughout most of the range of acid solutions, this metal is better than ordinary cast iron, sometimes—as in aerated dilute sulfuric—being as much as 100 times

* See chapter on Silicon Iron.

better. Figure 36,¹²⁰ carries corrosion rate data of this alloy in sulfuric at room temperature and hot, both at rest and agitated (mildly aerated). Tests in hot 90% sulfuric, both at rest and agitated, showed no advantage for the alloy over ordinary cast iron. It is particularly useful in dilute and very dilute acids. In intermediate concentrations, the attack is moderately high, as indicated for phosphoric in Figure 37. The rates for ordinary cast iron under similar conditions were 50 to 100 times greater.

Against strong acid-oxidizing conditions (e. g. dilute and intermediate concentrations of nitric, and acids carrying ferric salts) the alloy is not suitable.

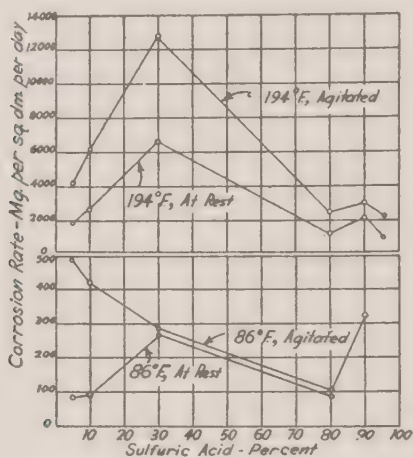


FIGURE 36. Alloy Cast Iron vs. Sulfuric Acid.

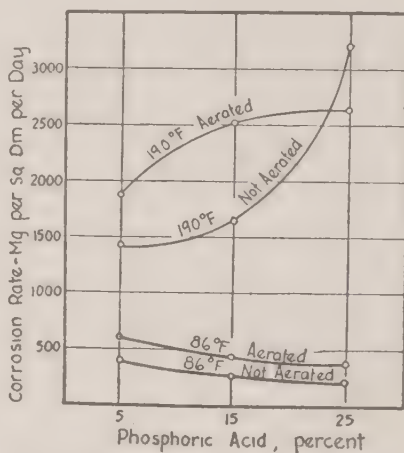


FIGURE 37. Alloy Cast Iron vs. Phosphoric Acid Under Constant Agitation.

Further comparisons between ordinary cast iron and this alloy cast iron are given in Table 141.⁶

TABLE 141.—Iron vs. Acids.

Acid	Conc. %	Time Hours	Temp. °F.	Mg. per sq. dm. per day	
				Ordinary Cast Iron	Alloy Cast Iron
Sulfuric	5 by vol.	120	68	12,000-14,000	27
	78 by vol.	4		6,200	3,200
Hydrochloric	5 by vol.	120-648	Room	4,400	25
Acetic	25 by vol.	168	Room	3,800	6.8

Alkaline Solutions.

In general, iron and steel are, for commercial purposes, resistant to alkaline solutions. In this group of substances are the hydroxides of sodium, potassium, barium and the alkaline salts such as sodium carbonate, silicate and phosphate. Aqueous solutions of these salts carry sodium hydroxide.

As already stated, iron is more resistant to alkaline solutions than to neutral. The boundary between the alkaline and neutral zones marking the first appearance of this greater resistance lies at a pH of 9 to 10. A very low concentration only of the stronger alkalies, such as sodium hydroxide, tri-sodium phosphate, and sodium silicate, is required to throw the solution on the alkaline side of this boundary. A somewhat higher concentration of the more weakly alkaline substances, as sodium carbonate and ammonia, is required, and the very weak alkalies like borax and di-sodium phosphate, even in substantial concentration, barely attain the "alkaline zone."

The relation between concentration of alkali and corrosion rate of steel is given in Table 142. In these tests, the solutions were open to the air at room temperature, and the duration was 22 days.⁶⁷

TABLE 142.—*Iron vs. Alkaline Solutions.*

NaOH Grams/liter	Mg. per sq. dm. per day	Ca (OH) ₂ Grams/liter	Mg. per sq. dm. per day
0	10	0	10
.001	9	.0013	9
.01	9	.013	8
.1	11	.13	6.5
1	.4	.67	0
10	.03	1.3	0
100	.08		
540	.03		

The resistance of iron to alkaline solutions is due to the development of a thin protective oxide film on the metal surface. Tests¹¹² have shown that neutral and alkaline solutions corrode iron in the first few minutes of exposure at practically the same rates, but that with time the rate drops more rapidly in the case of alkaline solutions. The data are plotted in Figure 38.

Conditions that may change the physical structure and adherence of this protective coating, or constituents in the solution that may have greater penetrating capacity, such as chloride, are causes of higher corrosion rates than the negligible rates ordinarily occurring in alkaline solutions. Aeration, elevated temperatures, the presence of dissolved carbon dioxide and of chlorides are accelerating conditions.

Actual corrosion rates of iron and steel in alkaline solutions at room temperature range under 1 mg. per sq. dm. per day. Very weak alkaline solutions corrode at rates intermediate between these, and the rates obtained in neutral solutions, or 10 to 20 mg. per sq. dm. per day.

The protective film that develops on ferrous metals in an alkaline solution is destroyed if the metals are withdrawn from the solution. Thus alternate exposure to alkaline solutions and either neutral solutions or the air will lead to rusting. Where rusting is undesirable, other metals are used.

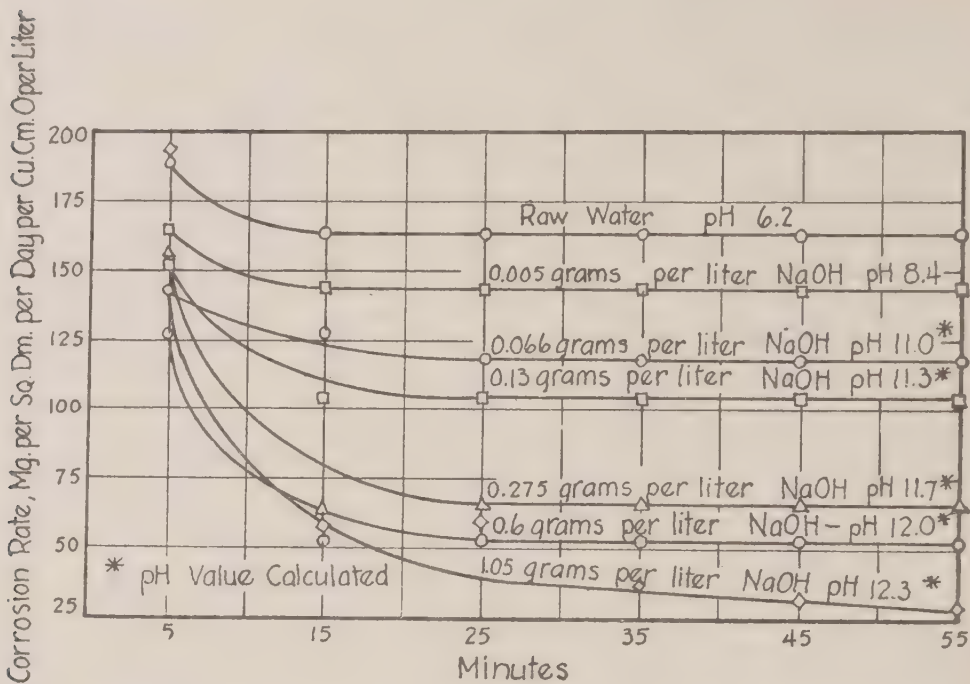


FIGURE 38. Steel vs. Air-saturated City Water with and without Caustic Additions, at 150° F.

In hot concentrated caustic solutions the protective film on ferrous metals is destroyed or at least damaged, and corrosion rates become relatively high. In spite of this, certain types of equipment for handling hot concentrated caustic are commonly made of heavy iron and steel construction. In the case of cast iron, and undoubtedly steel, resistance is materially improved by additions of nickel. A number of corrosion rates are listed below:

1. Submersion in evaporator concentrating caustic soda from 30 to 50%, at 179° F., for 380 hours. ⁷²
Steel 20 mg. per sq. dm. per day
Cast Iron 35 mg. per sq. dm. per day
2. Submersion in caustic soda during concentration from 32 to 52%, at 185° to 196° F., for 4¼ to 5½ hrs. under 660 mm. mercury average vacuum. ⁷²
Steel 3,500 mg. per sq. dm. per day
3. Submersion ⁹⁷ in vacuum evaporator during evaporation of (1.) caustic soda carrying originally 950 gm. NaOH and 12 gm. each NaCl and Na₂CO₃ per liter; (2.) caustic potash carrying 950 gm. KOH per liter—over temperature range from 320° to 750° F. for 6 hrs. (See Table 143.)
4. Submersion in evaporator concentrating caustic soda, made by the "ammonia-soda" process, from 50 to 65% under vacuum of 26 in., for 54 days. ⁷² (See Table 144.)

TABLE 143.—*Iron vs. Caustic Solutions.*

		Mg. per sq. dm. per day	
		Caustic Soda	Caustic Potash
Cast irons.....(unalloyed)		25-130	105-150
Nickel	3.06%	8.9	
Nickel	3.02%	12	15
Nickel	6.50%	9.3	10
Nickel	12.36%	.48	2.2
Chromium	3.09%	19	54
Chromium	7.27%	13	65
Chromium	11.58%	5.5	50
Nickel 5.86%, Chromium 4.88%		.48	1.4
Copper	3.95%	48	115
Copper	5.08%	35	160

TABLE 144.—*Iron vs. Caustic Solution.*

Cast Iron Nickel Content	Mg. per sq. dm. per day
0	366-458
3.5	235
5	247
15	152
20	17
20*	31
30	2

* Specimen carried 2% chromium.

Very high concentrations of caustic and fused caustic are severely corrosive to cast iron. Under these conditions, also, nickel is beneficial:

1. Rods rotated at high speed in caustic during concentration from 75% to anhydrous.⁷²

	Mg. per sq. dm. per day
Cast iron	6,660
Cast iron with 20% nickel	760
Cast iron with 30% nickel	680

2. Submersion in caustic carrying 5 to 10% water at 675° F. for 4 hours.⁷²

	Mg. per sq. dm. per day
Cast iron	5,979
Cast iron with 1.34% nickel	2,591
Cast iron with 3.54% nickel	2,118
Cast iron with 15.12% nickel	299

3. Submersion in anhydrous caustic at 675° F. for 4 hours and 24 hours.⁷²

	Mg. per sq. dm. per day	
	4 hrs.	24 hrs.
Cast iron	844	675
Cast iron with 2.91% nickel	707	619
Cast iron with 16.66% nickel	283	101

Hot moderately concentrated caustic solutions have a tendency to embrittle steel—a subject that has been discussed already.*

* See paragraphs under Boiler Corrosion.

Aqueous solutions of ammonia, although much weaker in hydroxyl-ion concentration than caustic alkaline solutions, have slight to no action on iron and steel. Ammonium hydroxide has the capacity of passivating iron completely. For instance, in aerated, agitated solutions ranging from .02 to 25% ammonia concentration, at room temperature, no faintest sign of corrosion took place.⁷² Ammonium chloride added to an 0.6% solution of ammonia caused localized attack; yet when added to a stronger solution—8%—the specimens again were passive. Strickland¹¹⁵ on the other hand found rates of 15 to 50 mg. per sq. dm. per day in an 8-day test in hot concentrated ammonium hydroxide.

The varieties of iron are widely used in storing and handling ammonia in aqueous solution, gaseous, and as moist vapors.

Two-Metal Galvanic Corrosion.

In galvanic behavior iron acts as an anodic (corroded) metal to copper, nickel, bronzes, brasses, chromium, stainless steels (usually), platinum, and as a cathodic (protected) metal to aluminum, zinc, and cadmium. Tin and lead are close to iron in electrochemical character; tin may be cathodic or anodic depending on factors such as aeration, and lead is usually cathodic.

As already pointed out the corrosion of iron by neutral solutions requires the presence of oxygen dissolved in the liquid. The coupling of cathodic metals like copper to iron increases the area of metal against which the cathodic oxygen reaction takes place, although all the dissolution of metal will still be confined to the iron. This feature of galvanic corrosion has already been discussed. In considering the galvanic behavior of iron particularly, it is convenient to keep it in mind, since iron in neutral solutions is susceptible to more pronounced two-metal galvanic attack than other metals.

Any neutral solution normally corrosive to iron will corrode at a greater rate when a cathodic metal is coupled with the iron. The point is illustrated by tests of Evans³⁹ in which strips of iron alone and coupled with cathodic metals were submerged in dilute sodium chloride for 14 days. The strips were 4 cm. by 2.5 cm. and were placed 2.2 cm. apart. The results are given in Table 145.

TABLE 145.—*Iron Couples vs. Sodium Chloride.*

	Contact Strip	Mg. per sq. dm. per day
None		27
Lead		34
Nickel		53
Copper		75

The degree of acceleration would have been much greater if the cathode areas had been larger, in accordance with the usual factors of galvanic action.

Evans³⁹ further made tests showing the acceleration of attack on iron by coupling with copper in both sodium chloride and tap water. The iron specimens had an area of 20 sq. cm. and a breadth of 2.5 cm., the copper cathodes were of equal and double area respectively. The tests were made at room temperature, and ran for 14 days. (See Table 146.)

TABLE 146.—*Iron: Copper Couples.*

	Mg. per sq. dm. per day	
	.1 N Sodium Chloride	Tap water
Uncoupled	27	13
Cathode breadth—2.5 cm.	75	16
Cathode breadth—5.0 cm.	114	21

The figures in Tables 147 to 150 indicate the order of galvanic attack of iron in couple with copper, in sulfuric and sodium chloride solutions, and the dependence of the attack on cathode surface treatment, on relative areas, and on total resistance.⁷²

TABLE 147.—*Iron: Copper Couples vs. Sulfuric Acid.*

Conditions: 5% sulfuric; iron anode (0.14 sq. dm.), copper cathode (3.3 sq. dm.); fully aerated, and agitated solution; 86° F.; 20 hrs., cathode finished with French emery #0.

External Resistance	Mg. per sq. dm. per day
Ohms	
.026	15,800
.026	17,800
.105	17,200

Note: Uncoupled corrosion rate of iron—1723 mg. per sq. dm. per day

TABLE 148.—*Iron: Copper Couple vs. Sodium Chloride.*

Conditions: 3% sodium chloride; iron anode (0.14 sq. dm.), copper cathode (3.3 sq. dm.); fully aerated, and agitated solution; 86° F.

	1.	2.	3.	4.	5.
Cathode treatment	French emery #0	French emery #0	French emery #0	Bright dip	Bright dip
External resist. ohms	0.105	0.105	0.223	0.223	0.223
Max. current amps.	0.0607	0.0705	0.0652		0.0628
Ave current amps.	0.0444	0.0374	0.0509	0.0544	0.0535
Hours	20	20	6	6	6
Equiv. wt. of iron in gms.	0.9218	0.7786	0.3221		0.3446
Actual loss in wt., in gms.	0.9198	0.7813	0.3183	0.3397	0.3342
Corrosion rate mg. per day	1106	934	1273	1357	1337
mg. per sq. dm. per day	7900	6600	9100	9700	9500

Note: Uncoupled corrosion rate of iron—350 mg. per sq. dm. per day.

TABLE 149.—*Iron: Copper vs. Sodium Chloride.*

Conditions: 3% sodium chloride; iron anode (0.14 sq. dm.), copper cathode (8.40 sq. dm.); fully aerated and agitated solution; 86° F. internal resist.—3.17 ohms.

Total Resistance Ohms	Current in Amperes	
	Observed	Calculated
3.41	.0525	.0529
5.41	.0413	.0409
7.41	.0333	.0333
9.41	.0279	.0281
13.41	.0213	.0214
23.41	.0135	.0134
33.41	.0101	.0098

TABLE 150.—*Iron: Copper Couple vs. Sodium Chloride.*

Conditions: 3% sodium chloride; iron anode (0.14 sq. dm.), copper cathode; fully aerated, agitated solution; 86° F.; resistance—3.41 ohms.

Cathode Area Sq. dm.	Anode Loss Grams	Time Min.	Current—Ampere	
			Observed	Calculated
1.01	.2267	1140	.0115	.0113
2.97	.5655	1085	.0300	.0276
5.16	.7920	1140	.0400	.0403
8.35	.9405	1095	.0495	.0527
10.00			.0577	.0575
11.63	1.0898	1095	.0572	.0615
18.50	1.2494	1080	.0666	.0728
infinite				.1058

These rates, both in sodium chloride and sulfuric, are exceptionally high due to the high order of aeration and agitation used in the tests.

In acid solutions the total corrosion of anodic iron, of course, is greater by virtue of the greater corrosiveness of the solution. In alkaline solutions the total rates are less than those in neutral, due to the milder corrosiveness of alkalies to iron. There may be no two-metal galvanic acceleration in the case of alkaline solutions at room temperature. Concentrated solutions at high temperature are very corrosive to anodic iron.

Two-metal galvanic relationships are important in the consideration of protective metallic coatings on iron. When the coating, usually very thin, is anodic to iron, the protection is good so long as no extensive surface of iron is exposed. When the underlying iron is anodic its exposure at pores and cracks may lead to pitting. Zinc and cadmium plate are ordinarily anodic and very effectively protective to iron in exposure to the atmospheres and waters. Nickel and chromium plate are cathodic, and pores in either lead to pitting of the iron. Tin and iron are so close in electrochemical behavior that the polarity may change with the slightest changes developing as corrosion progresses in the nature of the exposure conditions, these changes centering around the oxygen availability and the metal ion concentrations that build up at the metal surface. This oxygen availability is at once the most important, the most inconsistent, and the least readily measurable factor in two-metal galvanic as well as in ordinary corrosion.

From the practical standpoint the advisability of coupling iron with other metals in equipment depends on how much accelerated corrosion the nature of the design permits, on the oxygen availability and the degree to which the corrosion process is sensitive to changes in oxygen availability, on the electrical conductivity of the solution, and particularly on the relative areas of cathode and anode materials.

Another phase of two-metal galvanic corrosion has to do with action set up between two kinds of ferrous metals—e. g. cast iron and steel. Frequently the rivets on a ship are found more corroded than the plates fastened by them, but action of this sort is not necessarily galvanic in nature. It is more likely due to factors such as the poorer protection of paints on the extended rivet heads. That galvanic action between ferrous metals is possible, however, seems to be strongly indicated by Friend's data ¹⁰² on 5-year exposure periods. Mild steel rivets in a 14% chromium steel plate were almost completely gone, but in mild steel plates had not suffered accelerated attack in three locations out of four. In the fourth the rivets were badly attacked. In the case of coupled bars of equal area, wrought iron distinctly suffered accelerated attack, with corresponding protection of mild steel. In a steel and cast iron couple, the cast iron in three locations distinctly suffered, yet in the fourth the mild steel suffered. It is the nature of galvanic couples of metals closely similar in electrochemical behavior to have reversible polarity, the direction depending on characteristics of the corroding solution or the products of corrosion.

Bennett ¹⁵ has called attention to the fact that copper-bearing steel is cathodic to non-copper-bearing steel in sea water, even though, out of contact, the two behave similarly.

Galvanic action between mill scale and the clean surface of ferrous metals is suggested by Handy ⁶²; metal partially covered with mill scale had perforated by pits before clean metal on the same pipe had lost 20% in thickness.

HIGH-TEMPERATURE CONDITIONS

Iron, like most other metals, acquires a visible oxide coating at temperatures of 400° to 600° F. The coating is protective, the rate of oxidation increasing with time. Up to temperatures of about 1000° to 1100° F.³⁴ rates of oxidation are sufficiently low so that the metal is still useful. Above this range rates increase relatively rapidly, and the oxide coating furthermore is likely to scale off; for many purposes the plain irons and steels are not adaptable for continuous operation in oxidizing atmospheres. Because of low first cost and cheap replacement the metals are used in many cases at temperatures causing rather rapid oxidation. Even at 1300° to 1500° F.⁹⁹ the oxide that forms has some protective effect.

To illustrate the order of oxidation attack at different temperatures the results in Table 151 are given.⁶⁴ A mild steel was used, the atmosphere was ordinary air, and the duration 24 hours:

TABLE 151.—*Steel vs. Hot Oxidizing Gas.*

° F.	Gain Mg. per sq. dm. per day	° F.	Gain Mg. per sq. dm. per day
212	Nil	1292	1,190
392	3.3	1472	4,490
572	12.7	1652	5,710
752	45	1832	13,500
932	62	2012	20,800
1112	463	2192	39,900

These results unfortunately gave no inkling of the relation between time and oxidation. Other data⁹⁹ indicate, however, that at 1292° F. oxidation rates at the end of 6 hours have fallen off very considerably from those at the beginning of the 6-hour period, due to the protection of the oxide. The average oxidation rate over the first 24 hours would therefore be considerably greater than the rate at the twenty-fourth hour, provided that the oxide formed was truly protective. In any case 1000° to 1200° F. is generally considered the upper range of continued usefulness of iron and steel so far as oxidation is concerned.

Steam, carbon dioxide and carbon monoxide are oxidizing to iron at these elevated temperatures.^{30, 88} Steam breaks down in contact with iron at elevated temperatures with consequent oxidation of the iron and hydrogen evolution (see 46, 78, 100, 116, 117). At 1000° to 1100° F. the rate of oxidation through breakdown of the steam becomes rapid enough to be serious.^{53, 105, 110}

Sulfur dioxide is oxidizing as well and likely to be even more deteriorating,⁹² whether entirely through oxidation or through combined oxidation and sulfidation, than the other gases mentioned. A comparison of the action of different gases in 24 hour exposure at 1292° F. is given in Table 152.⁶⁴ Sulfur dioxide was no more corrosive under these conditions:

TABLE 152.—*Iron vs. Hot Oxidizing Gas.*

	Gain—Mg. per sq. dm. per day			
	Oxygen	Steam	Carbon Dioxide	Sulfur Dioxide
Pure iron	5111	6223	5873	3540
Mild carbon steel	1042	365	1002	985
3% nickel steel.....	4003	869	984	3019
Cast iron	1177	2261	1395	675

Reducing gases carrying sulfur are strongly deteriorating. In 160-hour tests¹²⁶ at 932° F. and atmospheric pressure, hydrogen sulfide attacked mild steel at the following rates:

	Mg. per sq.
Dry	dm. per day
	2,350
Moist	2,050

No slowing down of rates with time was noticeable.

Oxidation rates and scaling tendency in the temperature range above 1200° F. become problems in the heating of iron and steel preparatory to hot working and in heat treatment. Work on these problems has aimed to outline scaling rates and the modifications in heating atmosphere that may be used to suppress scaling (see References ^{17, 92}). A curve covering the loss in weight in exposure for one hour to air is given in Figure 39 for low carbon steel.⁸⁷ Heating in non-oxidizing atmosphere is a preventive of scale losses.

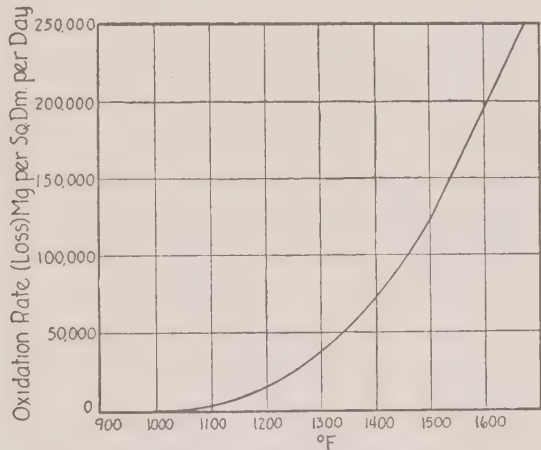


FIGURE 39. Steel vs. Air at High Temperature.

The investigations of Pilling and Bedworth⁹⁹ and of Pfeil⁹⁸ have sought an explanation of the mechanism of oxidation in the higher temperature range.

Irons and steels absorb carbon and nitrogen under suitable heat conditions. On this capacity is based the processes of case-hardening (carburizing) and nitriding of steels, in which the steel acquires a hard surface. In the former steel is exposed to carbon or gaseous carbon compounds at 1500° to 1900° F. In nitriding, steel of suitable composition, exposed to ammonia at 900° to 1000° F., breaks down the ammonia and absorbs the nitrogen.²⁷

In ammonia mixtures, either cracking or synthesizing, steel and iron undergo over a period of time an intercrystalline deterioration.^{119, 121} The rate of decomposition of ammonia is very slow below 570° F., but at 850° to 1200° F. the rate is rapid. Exposure of a few hours, or at most 24 hours, in a current of ammonia at about 1200° F. will destroy the usefulness of the metal for many structural purposes.

Cast iron is subject to a type of deterioration known as “growth.” With repeated heatings at elevated temperatures the iron increases in volume, sometimes as much as 40 to 50%. The degree of growth increases with temperature and is in addition much greater above the critical temperatures for the iron than below. Results of a recent investigation on growth are given in Figures 40 and 41.¹³⁴

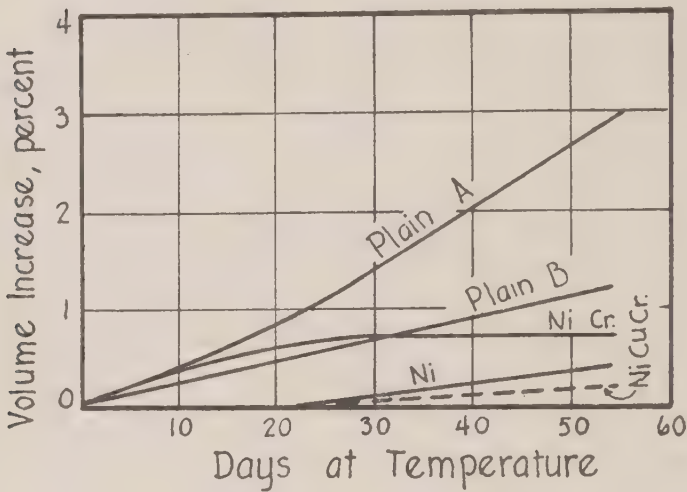


FIGURE 40. Growth of Cast Iron in Steam at 900° F.

	TC	Si	Ni	Cr	Cu
Plain A	3.48	2.02			
Plain B	3.36	0.82			
Ni Cr	3.04	1.39	0.96	0.33	
Ni	2.89	2.45	1.45		
Ni Cu Cr	3.04	1.64	13.6	3.23	6.48

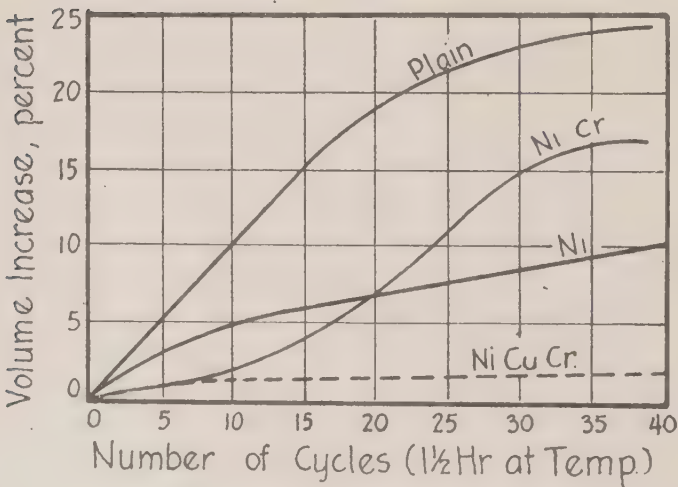


FIGURE 41. Growth of Cast Iron in Carbon Dioxide at 1500° F.

	TC	Si	Ni	Cr	Cu
Plain	3.26	2.02			
Ni Cr	3.43	1.08	2.33	0.49	
Ni	3.82	0.45	3.97		
Ni Cu Cr	2.88	1.72	14.31	3.92	5.37

Growth at temperatures above about 1300° F. is ascribed generally to graphitization of the combined carbon, the oxidation of the silicon-iron matrix, and the expansion of occluded gases. In the lower temperature range growth is due to decomposition of the combined carbon into ferrite and graphite, and, in Wood's ¹³⁴ opinion, to some other factor, possibly to internal oxidation or to occluded gases.

Molten metals are handled usually in cast iron and steel. Attack takes place, but relatively slowly, and the use of the metals is usually economical. In handling lead, cast iron is used for the most part below 1300° F. and steel above this temperature.¹⁰⁷ Strong corrosion by lead has been traced to the action of lead oxide.

The alloying action of zinc on iron becomes strong at 860° F. and gradually increases in intensity to 900° F. Above 900° F. continued operation will destroy a pot in three days if the heat is highly localized.⁷¹ Daniels ²⁹ sets 900° F. as the "critical temperature which must not be exceeded if kettles are to be in use for a long period without replacement." Below this temperature a solid zinc-iron compound forms a highly protective coating, but above 930° F. this breaks away. He has given the relation in Table 153 between temperature and life of a 1.5-inch thick kettle.

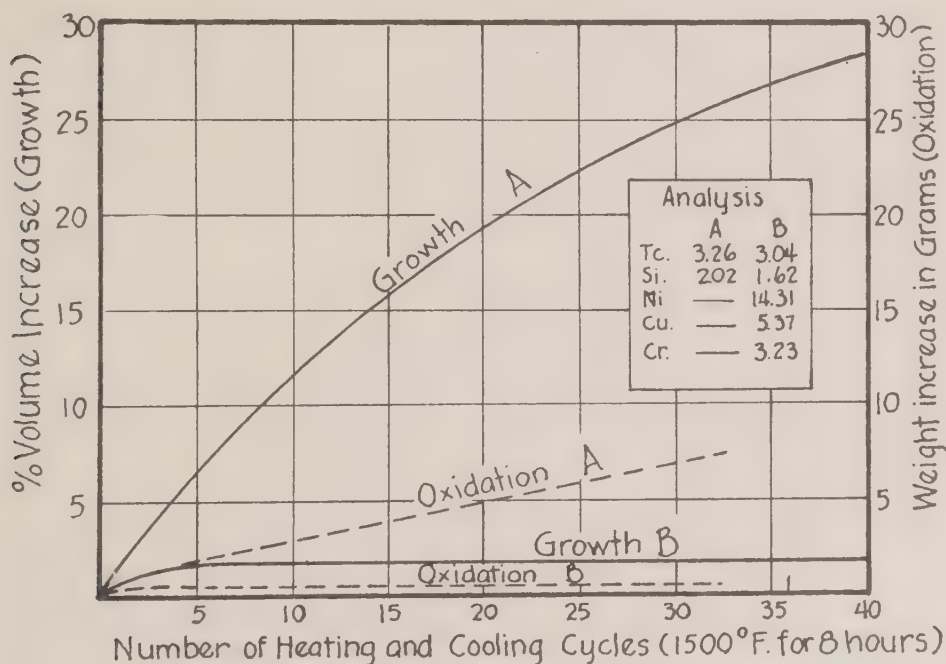


FIGURE 42. Cast Iron vs. Air at 1500° F.

Other molten metals may be damaging to iron and steel. Genders ⁵⁴ has studied the problem of fracturing of steel when exposed under stress to

TABLE 153.—*Iron vs. Molten Zinc.*

° F.	Life
810	2410 years
890	1487 years
932	28.1 days
1004	19.6 days

molten brazing solder and copper, and others¹⁰⁸ have demonstrated the same effect with other melts. Avoidance of stress seems to be a preventive of cracking under these conditions.

Improved heat resistance of iron and steel is gained by alloying. Additions of chromium and nickel are treated in another chapter. Iron and steel whose surface has been treated at high temperature with aluminum is useful up into the 1500° to 1600° F. range,¹⁰⁶ and particularly for sulfur-bearing gases. Cast iron alloyed with nickel, copper and chromium has considerably better resistance to both growth and oxidation than ordinary cast iron, as shown in Figure 42.¹²⁰

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Chapter XII

Silicon-Iron

Although limited in usefulness by low tensile strength and hardness, silicon-iron alloys carrying 13 to 15% silicon are important for unusually effective resistance to acid corrosion. Produced in cast form only, these alloys are so hard that in most cases ordinary machining operations cannot be applied. In spite of this drawback silicon-iron equipment is rather widely used for special purposes in the chemical plant.^{4, 6, 14, 20, 21, 23}

In acid exposure of both oxidizing and non-oxidizing character the silicon-iron alloys have perhaps better intrinsic resistance than any other type of metal. This is particularly true of the more active acids like nitric, sulfuric and phosphoric.

Increasing silicon in iron progressively improves corrosion resistance to acids, but really useful behavior is not attained until the silicon content reaches 13 to 15%. It is generally believed that these alloys acquire in exposure a superficial but extremely protective surface layer of silica. Unfortunately the resistance of these is gained only with the nearly complete loss of ductility.

A fair body of corrosion data exists on silicon iron.^{1, 2, 3, 5, 6, 7, 9, 11, 13, 15, 17, 22} On examining them critically two facts stand out—the remarkably low order of minimum attack in exposure to strong acids like sulfuric and nitric, and the great scatter of rates over a range above this minimum.

Two reasons account for the scatter. The first is the fact that the alloys tested range from 13 to 15% silicon, and so strong is the effect of silicon content as a factor in determining resistance that a difference in corrosion rates of a thousand times or more may exist between a 13% and a 15% silicon casting. An example of this is the result in Table 154 of tests where specimens were immersed 98 to 135 days in flowing acid mine water,¹⁸ at room temperature.

On the other hand it is a fact that when a commercial alloy is held consistently to a definite silicon content—as 14.35 to 14.65% silicon, which is true of the product of one manufacturer—the resistance becomes consistent.

TABLE 154.—*Silicon-Iron vs. Acid-Oxidizing Mine Water.*

Water composition		Mg. per sq. dm. per day	
Substance	%	13-14% Silicon	14-14.5% Silicon
Sulfuric21		
Ferric iron09	490	.4
Sulfuric14		
Ferric iron006	272	.04
Sulfuric04		
Ferric iron014	222	.2

The second reason for the scatter of rates is that corrosion rates of silicon-iron in strong acids characteristically decrease with time over the first few hours exposure. For this reason rates over an 8-hour period or a 24-hour period, for instance, are much higher than those covering longer periods. Thus rates in 120-day tests have ranged down below 1 mg. per sq. dm. per day in acids that in 8-hour tests have given rates on the order of 100 to 300 mg. per sq. dm. per day. It is obvious that the higher rates over the first day or two of exposure will not be damaging if the subsequent or long-time rates are as low as 1 mg. per sq. dm. per day.

Perhaps the most significant set of corrosion data are those obtained by the National Bureau of Standards⁵ covering 100-days exposure in cold unagitated acid. The following substances gave average corrosion rates over this period of less than 1 mg. per sq. dm. per day: sulfuric—10, 25, 95%; nitric—10, 25, 70%; acetic—99%; phosphoric—10, 25, 87%; oxalic—2, 8%; picric—9%; ferric chloride—7, 48%; commercial oleic acid; pyrogalllic acid. Hydrochloric acid was, on the other hand, more corrosive; a 5% solution gave a rate of 15 mg. per sq. dm. per day, and 25% acid a rate of 40 mg. per sq. dm. per day.

These results are particularly useful in that they correspond rather closely with actual experience. As a general, if not invariable, rule silicon-iron has extremely good resistance to solutions at ordinary temperatures of all acids except hydrochloric, hydrofluoric, other halide acids, and sulfurous. Rates after development of the protective film fall below 10 mg. per sq. dm. per day, ordinarily below 1 mg. per sq. dm. per day.

An important point to note is that oxidizing acids as well as non-oxidizing are included in the non-corrosive group. Thus, acids that are intermediate between the two types may be satisfactorily handled. Such acids are inclined to be corrosive to the copper group of metals because of too high oxidizing capacity, and corrosive to the chromium alloys because oxidizing capacity is not sufficiently powerful to give passivity. Phosphoric, sulfuric, and aluminum sulfate solutions, with low ferric iron content, are typical.

Hydrochloric, as stated, is corrosive to silicon-iron. Short time tests give rates on the order of 300 to 1,000 mg. per sq. dm. per day, the very

long time test results quoted above are 15 to 40 mg. per sq. dm. per day. Intermediate rates are perhaps more typical. A special silicon-iron composition, carrying 3.5% molybdenum, has been developed for hydrochloric. Corrosion rates in 15 to 30% acid at 176° F. have been given as 100 to 300 mg. per sq. dm. per day, which as compared with other metals must be considered good useful resistance to this extremely corrosive condition. These particular rates applied to exposure following previous 48-hour exposure, so that it may be considered fair average behavior.⁵ In other tests,¹³ in concentrated acid at room temperature, a rate of 90 mg. per sq. dm. per day was obtained at the end of 24-hours exposure, and an average rate of 20 mg. per sq. dm. per day over a subsequent 12-hours exposure. The slowing down of the rate was due to protective film formation.

According to the National Bureau of Standards tests quoted above ferric chloride was mild in its action compared with hydrochloric. The oxidizing capacity of the ferric iron is in this case definitely beneficial; in general, it may not be beneficial, but it is not harmful. Silicon-iron has good resistance also against other acid-oxidizing solutions such as tin chloride. This behavior is interesting in view of the fact that with chromium alloys not even ferric iron, or stannic tin is a strong enough oxidizer to bring about passivity in acid chloride solutions.

Elevated temperatures are accelerating with some solutions. Hot solutions of either acetic or nitric have little or no accelerating effect, and hot solutions of sulfuric and the large majority of acids are not as a rule seriously corrosive. Hot hydrochloric and other halide acids are of course entirely out of the question for ordinary high silicon-iron, but the molybdenum-bearing alloy is claimed to be serviceable at least in hydrochloric. Hot ferric chloride is rapidly corrosive to ordinary silicon-iron; its effect on the molybdenum modification has not been outlined.

One set of data covering behavior in hot acids is interesting. Silicon-iron submerged in aerated phosphoric solutions at 206° F. for 24 hours (or more) gave the results in Table 155.⁸

TABLE 155.—*Silicon-Iron vs. Phosphoric Acid.*

Concentration %	Mg. per sq. dm. per day
Pure	
50	36
25	7.5
10	29
Crude	
dilute	700

The crude, dilute acid carried hydrofluoric acid and ferric iron. In view of the damaging effect the former has on silica it is presumed that this accounts for the strong attack.

Sulfurous acid is variable in its corrosiveness to silicon-iron. Certainly caution must be exercised when considering the use of silicon-iron in handling this acid. In one set of tests¹⁰ rates ranged from 900 to 1200 mg. per sq. dm. per day in calcium bisulfite solutions carrying $3\frac{1}{2}$ to $4\frac{1}{2}$ % free sulfurous at 295° F. under pressure. These conditions of course are extremely severe.

The electrochemical behavior of silicon-iron is determined largely by the silica protection film. Acting as an anode with an impressed current, the alloy has had extremely high corrosion resistance in acids¹⁶ and in cyanide.¹⁹ Richardson¹² has reported that in sulfuric, nitric, sodium sulfate, and acetic, silicon-iron had a potential difference with aluminum of practically zero. Coupled with iron in sodium chloride, silicon-iron was at first strongly cathodic, becoming much less so with time. In dilute sulfuric silicon-iron was at first cathodic, slowly to become anodic.

The presence and effect of this film is commented on by Fink*: "such an electrode (silicon iron used as an anode) has upon its surface, a chemically inert, thin, enshrouding film of low electrical resistance which prevents the mechanical diffusion of ions to its surface where oxidizing or reducing action will take place. An examination of the silicon-iron electrode surface clearly demonstrates the presence of this porous film, direct analysis of which has shown it to be composed substantially of silicon dioxide." Silicon-iron anodes are used for this purpose in the Bullard-Dunn process for cleaning metals where, typically, the bath is a 10% sulfuric acid solution, with tin or lead salts present. Some of the first installations of silicon-iron electrodes in this process were in use at the end of two years.

Alkaline solutions, particularly caustic solutions but also even mildly alkaline ammonium hydroxide, are corrosive to silicon-iron. On no account is the alloy serviceable in these.

Though probably of reasonably good resistance to neutral solutions, if not excellent resistance, silicon-iron as compared in all-round characteristics with cheaper and more flexible materials has no virtue for handling them.

* U. S. Patent 1,927,116.

SILICON-IRON

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Chapter XIII

Molybdenum Alloys

GENERAL

Molybdenum as an alloying element is important in the field of corrosion resistance. The chapter covering chromium alloys carries data on the beneficial effect of low contents of molybdenum in the chromium-nickel-iron alloys against certain of the acids, particularly hydrochloric and sulfurous acids.

This present chapter will deal with two alloys that owe, in large measure, the definite merit they possess to their molybdenum content. One alloy carries 60% nickel, 20% molybdenum and 20% iron, and is a wrought product. The second, more complex, carries, nominally, 58% nickel, 17% molybdenum, 14% chromium, 5% tungsten, and 6% iron, and is available only in casting form, of good toughness. Both alloys are widely corrosion resistant, in the sense that the copper and the nickel group of alloys, and the chromium alloys are. In addition these two compositions are far more resistant than the other groups to hydrochloric acid solutions.

Hydrochloric is one of the most corrosive of the acids. The chromium alloys are rapidly reactive with it. The nickel and copper metals cannot be considered commercially resistant to it when aerated, hot, or in concentrations higher than perhaps 10%. Furthermore lead and aluminum are not useful with it. These molybdenum alloys are particularly and very usefully resistant to hydrochloric acid.

The simpler alloy—60 Ni 20 Mo 20 Fe—is more resistant than the other against non-oxidizing acid solutions and far less resistant than the other against oxidizing acids. This is the principal distinction in behavior between the two compositions. Thus the simpler alloy gives no satisfaction in contact with nitric acid, or acid solutions carrying ferric or cupric or tin salts, yet in these the more complex alloy is very definitely resistant.

HYDROCHLORIC ACID

Although pure nickel is one of the more resistant of the common metals against hydrochloric, still in all but cold dilute solutions it cannot be

considered useful. Molybdenum added to nickel brings about a very substantial improvement, as indicated by the curve given in Figure 43. The acid was of 10% concentration, at 158° F.¹

Further tests, at the same time, brought out the fact that iron to the extent of 20%, along with 20% molybdenum, did not lessen resistance in any appreciable degree.

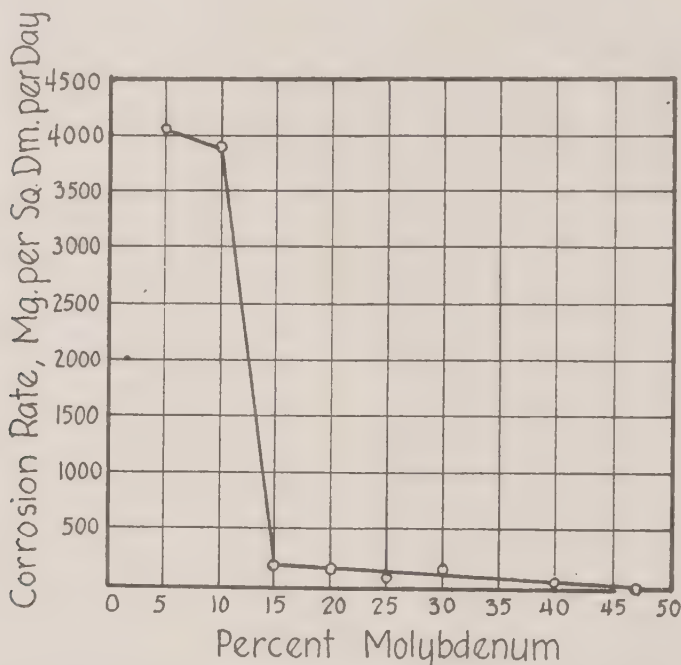


FIGURE 43. Nickel-Molybdenum Alloys vs. 10% Hydrochloric Acid at 158° F.

In all concentrations of unaerated hydrochloric at room temperature, 60 Ni 20 Mo 20 Fe is corroded at rates ranging below 25 mg. per sq. dm. per day. This may be considered excellent resistance. With aeration, however, the attack is accelerated very markedly, particularly in concentrations of 1 to 10%. Figure 44, illustrating the effect of aeration, has been taken from the data of Rohrman.⁵

Data on both types of molybdenum alloy are given in Table 156.* Although there does not appear to be much difference between the alloys in quiet acid at room temperature, the simpler alloy is decidedly better in the warm and boiling solutions. The duration of test is not known.

Tests have been made³ with specimens submerged 2800 hours in a 10 to 12% hydrochloric acid in use as a pickling solution for iron, at a

* B. E. Field, private communication.

FIGURE 44. 60 Ni 20 Mo 20 Fe vs.
Hydrochloric Acid.

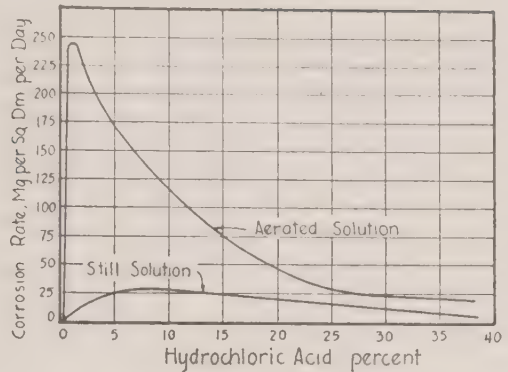


TABLE 156.—Molybdenum Alloys vs. Hydrochloric Acid.

	Corrosion Rate—Mg. per sq. dm. per day	
	60 Ni 20 Mo 20 Fe	Complex Alloy with Cr, W
Room temperature, quiet		
10%	14	14
37%	2	5
158° F., aerated		
10%	144	190
15%	190	720
25%	144	480
37%	120	500
Boiling		
10%	1870	3840
15%	1840	4100
25%	1960	3600
37%	1600	1900

temperature of 70° to 90° F. Both types of alloy were corroded at rates of about 30 mg. per sq. dm. per day.

Data bringing out the much better behavior of the alloy carrying chromium and tungsten, in an oxidizing hydrochloric acid solution, are given in Table 157.³ The solution was 45% ferric chloride and the specimens were alternately dipped into the solution and withdrawn. The duration is not known.

TABLE 157.—Molybdenum Alloys vs. Ferric Chloride.

	Mg. per sq. dm. per day
60 Ni 20 Mo 20 Fe	45,000
Complex alloy	58

In another test samples were exposed in the sludge filter effluent of a sewage disposal plant, the solution carrying 0.2 to 0.5% ferric chloride. (See Table 158.)

TABLE 158.—Molybdenum Alloys vs. Ferric Chloride.

	Mg. per sq. dm. per day
60 Ni 20 Mo 20 Fe	96
Complex alloy	0.3

Elevated temperatures seem to accelerate considerably the action of oxidizing acids on both alloys. In 10% hydrochloric acid carrying 10% by weight of added cupric chloride, at 158° F., the rates for both were well above 20,000 mg. per sq. dm. per day. When ferrous chloride was added, rather than cupric chloride, the rates were about 600 mg. per sq. dm. per day. The complex alloy was also tested with ferric chloride as the added salt, the rate being 1300 mg. per sq. dm. per day. The good behavior of the complex alloy in oxidizing hydrochloric acid does not appear, therefore, to extend into the hot range.

SULFURIC ACID

Data on the action of sulfuric acid on these alloys are given in Table 159.*

TABLE 159.—Molybdenum Alloys vs. Sulfuric Acid.

Corrosion Rate—Mg. per sq. dm. per day		
60 Ni	20 Mo	20 Fe Complex alloy
Room temperature, quiet		
10%	16	< 1
25%	10	< 1
60%	2	—
77%	—	—
96%	< 1	< 1
158° F., aerated		
10%	160	23
25%	75	50
60%	75	75
77%	75	50
96%	18	3
Boiling		
10%	210	310
25%	300	300
60%	3,000	5,500
77%	13,000	10,000
96%	1,300	5,000

The addition of 10% ferric sulfate to 10% sulfuric acid, at 158° F. led to strongly accelerated attack of both alloys, as compared with the figures in Table 207 for the same conditions.

Tests have been made on these alloys in the highly impure water of smoke scrubbers, both in a steam power plant and in a steam locomotive terminal.³ These solutions are hot, perhaps 120° to 140° F., and carry as the principal corrosive substances sulfuric, sulfurous, and hydrochloric acids, and ferric iron. The condition, then, is an acid-oxidizing one, and consequently the nickel-molybdenum-iron alloy carrying chromium and tungsten gives better behavior than the simpler composition. In fact the complex alloy was found to have a much higher degree of resistance than any of the other metals tested. A number of rates are given in Table 160.

* B. E. Field, private communication.

TABLE 160.—*Molybdenum Alloys vs. Oxidizing-Sulfidizing Acid.*

	Corrosion Rate—Mg. per sq. dm. per day	
	60 Ni 20 Mo 20 Fe	Complex alloy
Effluent from scrubber, power plant		
263 hours	7	3
45 days	36	0
In scrubber, power plant		
35 days	128	6
In scrubber, locomotive		
100 days	206	

These results indicate that the complex alloy probably would have good resistance to sulfidizing conditions, though no data other than these are available to prove it. The combination of sulfurous acid and chlorides makes a very strong corrosive, and the authors know of no other alloy that is really useful for handling it.

NITRIC ACID

In nitric acid the 60 Ni 20 Mo 20 Fe alloy is rapidly attacked, as it is in any acid-oxidizing solution. The complex alloy with chromium and tungsten, on the other hand, has fairly good resistance though not so good as the better grades of stainless steels. In Table 161 are given rates for the complex casting alloy.*

TABLE 161.—*Molybdenum Alloys vs. Nitric Acid.*

Per Cent Concentration	Corrosion Rate—Mg. per sq. dm. per day		
	Room temp.	158° F.	Boiling
10	80	250	275
20	—	330	1100
30	—	475	—
40	—	830	—
50	60	900	—
60	—	1000	—
70	30	820	13,000

PHOSPHORIC ACID

Hot aerated pure phosphoric acid and hot crude acid are far more corrosive to the 60 Ni 20 Mo 20 Fe alloy than to the complex alloy carrying chromium and tungsten. Crude phosphoric acid carries ferric iron, which makes it oxidizing. The rates in Table 162 were obtained in acid at 176° F., the duration being 24 hours or greater.⁴

* B. E. Field, private communication.

TABLE 162.—*Molybdenum Alloys vs. Phosphoric Acid.*

	Corrosion Rate—Mg. per sq. dm. per day		
	60 Ni	20 Mo 20 Fe	Complex alloy
Pure acid, aerated			
10%		700	48
25%		530	40
50%		240	17
Crude acid			
Dilute, aerated		4300	90
Concentrated, not aerated		2000	64

Aeration probably made the pure acid more corrosive to the simple alloy, and perhaps less corrosive to the other.

WET CHLORINE

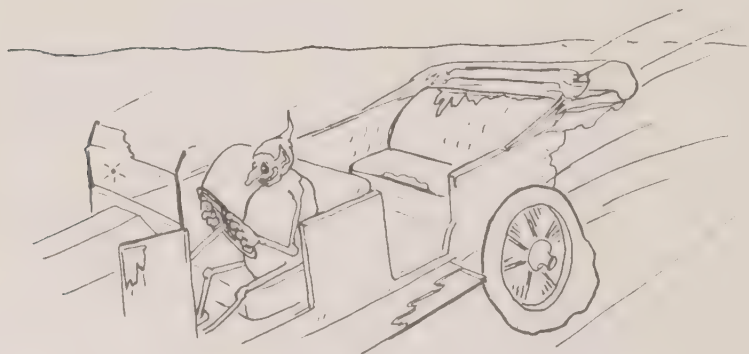
Wet chlorine is a particularly corrosive substance. It is stated * that the complex casting alloy, carrying chromium and tungsten has good resistance against this condition. A single rate, 240 mg. per sq. dm. per day, has been obtained. The 60 Ni 20 Mo 20 Fe alloy is not useful with wet chlorine.

* B. E. Field, private communication.

MOLYBDENUM ALLOYS

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Chapter XIV

Chromium Alloys

Chromium confers on its alloys with iron and nickel a degree of resistance to corrosion and high heat, under a large range of conditions, not equalled by other metals.*

At the present state of development of the series the principal "nucleus" alloys are as follows:

Corrosion resistant

18 Cr 8 Ni bal. Fe
12-18 Cr bal. Fe

Heat resistant

12-20 Cr 60-80 Ni bal. Fe
15 Cr 35 Ni bal. Fe
30 Cr 15 Ni bal. Fe
28 Cr bal. Fe

Innumerable variations of these are produced commercially, and a considerable degree of interchangeability in properties among these groups exists.

CORROSION-RESISTANT ALLOYS

For substantial useful rust resistance the chromium content of the chromium-iron alloys must be around 12% or greater, resistance against the broadest range of conditions being attained in this alloy group with perhaps 20 to 30% chromium. These chromium-iron alloys have a wide utility, yet certain limitations appear in the processes of production and working, and also in mechanical properties. The 12 to 18% chromium alloys, if the carbon:chromium ratio is greater than a definite minimum, must be properly heat treated to bring about the best degree of rust and corrosion resistance; this fact is well recognized and is rarely a limitation.

Nickel in this group, in sufficient ratio with the chromium, has as its principal effect the development of austenite; austenite is characterized by better all-round mechanical properties, particularly toughness. From the corrosion standpoint likewise nickel contributes important benefits, to be brought out later.

In the 18-8 composition, the 18% content of chromium is considered sufficient to give the full benefit of chromium to corrosion resistance and the 8% nickel to give the austenitic structure, with its favorable mechanical

* Excellent books on the chromium alloys are those of Monypenny⁶⁰ and Thum.⁹⁵

properties, and further improvement in corrosion resistance. In Europe other austenitic alloys*—13 Cr 13 Ni, 15 Cr 10 Ni, 20 Cr 7 Ni—are widely used for general corrosion-resistant purposes.

HEAT-RESISTANT ALLOYS

Alloys for handling high heat developed originally with chromium additions to nickel rather than to iron. One of the early compositions, 20 Cr 80 Ni, is still considered the most suitable for the highest heat. Dilution of this with iron was found to give good results at temperatures almost to the safe limit for 20 Cr 80 Ni, and so 15 Cr 60 Ni 25 Fe developed. Later in the interests of cost and better resistance to sulfidizing substances, further iron was substituted for nickel, the series including the nickel-free 25-30 Cr Fe as the other limit.

It is obvious that the alloys used principally for handling heat will have useful corrosion-resistant properties, and the 18-8 and chromium iron series very considerable value at elevated temperatures. The discussion that follows first considers corrosion and then goes on to cover the effect of heat.

PASSIVITY—ACTIVITY

The outstanding individual property of chromium alloys is the capacity to be passive. The range of solutions in which passivity takes place is a very broad one, yet, with many solutions there is a point, as the conditions become more severe, where a slight change in some condition—increase in temperature, decrease in oxidizer, or change in concentration—throws the metal from a state of passivity to one of activity. In general the chromium alloys in the active condition are rapidly corroded, in the passive condition virtually unattacked or relatively slowly attacked. The passivity-activity boundary, shifting often with delicate changes in exposure condition and likewise with delicate changes in the composition and structure of the alloy, becomes in a sense the limit of usefulness of the alloy.

As an example, a boiling sulfuric acid solution of .02% concentration and less is passivating to 24 Cr 10 Ni,⁶⁷ with corrosion rates of less than 1 mg. per sq. dm. per day. On the other hand concentrations of .05% and greater are activating, with rates of 200 mg. per sq. dm. per day and greater.

* Austenite in these alloys as well as in 18-8 is not the stable condition at ordinary temperature, but is retained down to ordinary temperature by rapid cooling from the temperature range within which it is stable. Martensite and austenite are equally corrosion resistant. The rapid cooling that retains the austenite has the very important effect, as discussed later, of preventing carbide formation, since precipitation of carbide lessens resistance. Cold-working of a fully austenitic alloy will develop martensite, without lessening resistance.

Again, in boiling 65% nitric acid, 18 Cr 8 Ni .08 C, quenched at 1800° F., was corroded at a rate of 60 mg. per sq. dm. per day, yet when quenched at 1800° and drawn at 1200° the rate was 2800 mg. per sq. dm. per day.⁵⁵

Still again; in concentrated (1.2 spec. grav.) nitric acid, 7.5 Cr Fe and alloys with higher chromium content are passive with rates under 12 mg. per sq. dm. per day, whereas with 4.7% chromium and less rates are over 2000 mg. per sq. dm. per day.⁶⁰

Finally there is the case of two alloys of the same composition—17 Cr Fe —, one remaining fully active, the other fully passive in a very dilute, boiling sulfuric-nitric solution. The active metal failed rapidly when used to line a container, yet the passive metal stood up indefinitely. The reason why one alloy remained passive while the other was active escaped discovery at the time.

In the examples just cited the passivity-activity boundary may be viewed as a very narrow zone separating good behavior of the alloy from poor. Often this boundary is a broader zone wherein exposure conditions seem to be neither fully activating nor fully passivating. Thus ⁴² the potential of 18-8 in two series of measurements in air-saturated salt solution of high concentration persisted over a 50-hour period at a value intermediate between those characteristic of fully active and fully passive 18-8.

Some exposure conditions are so effectively passivating that a few per cent of chromium only is necessary for passivity. Concentrated nitric is an example; in 35% acid 10 Cr Fe is passive. Others are so strongly activating that none of the variations of stainless so far developed become passive in them. Concentrated hydrochloric is an example.

Of the chromium alloys, the passivity range of 18-8 and its variations is as extensive as any. It is on this that the widespread use of the alloy is based. Yet with many substances with which it is successfully used there are limits to its passivity, and the boundary zone must be kept in mind. Any strong acid solution when of low oxidizing power activates it. Neutral solutions like sea water will activate it in the presence of special concentration cells of the kind set up, for instance, by barnacle adherence or by pores in welded metal. Even in outdoor high sulfur and marine atmosphere, local activation and pitting often develop at the crossing of wires in a window screen.

The general picture of passivity phenomena suggests the complexity of chromium alloys in corrosion behavior. Without the first step towards simplification afforded by the concept of a passivity-activity boundary, the problem would indeed be a most difficult one. It is well to note here that with other metals passivity is a very minor concern if existent at all. Changing exposure conditions in the case of these other metals leads only

to proportionate changes in corrosion resistance, without the very marked difference that occurs with stainless when the boundary is crossed.

We shall now attempt to bring out some of the more important implications of passivity-activity, first those dealing with the exposure condition and then those concerned with the metal itself.

Early in the development of stainless it was believed that a passivating treatment in concentrated nitric would give stainless a resistance against otherwise activating solutions. The original thought has been somewhat revised since no passivating treatment has been found which produces permanent effects in solutions which are activating. Passivating treatment may delay corrosion under activating conditions and is useful in hastening and making passivity more complete when used in mildly passivating solutions. However, passivated metal will become active under activating conditions, even though first tests may show it to be completely passive.

Another point worth bringing out is that the passive metal is passive in a relative sense only—actually corrosion is going on, though often extremely slowly. Passive metal in strong hot acid solutions may have rates of 15 to 20 mg. per sq. dm. per day, whereas active metal will corrode at rates of several thousand. Passive metal in the atmosphere may corrode enough to form an extremely fine superficial layer of iron rust, if indeed it corroded to a visible extent, whereas active metal will lose its surface within a year or two.

Since even passive metal is corroding, maintenance of passivity requires the continuous replenishment of the agent—i. e. oxidizing substance—that produces it. As an example—in ordinary sea water the dissolved oxygen in the water is sufficient to maintain passivity, whereas beneath a barnacle or other properly adherent substance, metal becomes active since the rate of oxygen replenishment is too slow to maintain passivity. Activation and pitting result.

Still another important point is that when corrosion of the chromium alloys does take place the action is often localized. This is particularly true when the exposure conditions are passivating yet on the border line of being activating. The simplest case is illustrated again by activity established beneath an adherent deposit. At any rate when once a pit starts and so long as the localized activating condition persists, a concentration cell is set up with the metal surrounding the pit becoming cathodic. This cell becomes extremely intense in good electrolytes, since the area of effective cathode becomes very large as compared with the anodic pit. A penetration rate as high as one inch per year has been observed beneath a deposit in sea water exposure.

Factors within the metal that are important determinants of the passivity range are equally as complex as those in the exposure condition. Chromium

content of course is the most important single consideration. Increasing chromium, other things being equal, invariably broadens the passivity range. The maximum benefits are derived at 25 to 30% chromium in the non-nickel-bearing alloys, and 18 to 30% chromium in the nickel-bearing austenitic alloys.

Carbon content is an extremely important consideration. A carbon content cannot be avoided in these alloys, yet it can be held so low that, with proper heat treatment, no disadvantage results. It becomes damaging when present as a precipitated chromium carbide. The chromium content of the carbide is sixteen times the carbon content, and is derived from the iron-chromium solid solution. The difficulty enters in when withdrawal of chromium from the solid solution has gone on to the extent that the chromium remaining in the solid solution is less than roughly 11%, for then the alloy is no longer broadly passive. The distribution of chromium-depleted zones is a function of the *loci* of carbide precipitation. In the ferritic (straight) chromium steels, the precipitation is generally, though not always, at random, giving rise to a fairly general chromium depletion of low intensity. In the austenitic chromium steels, except where cold-worked, the precipitation is largely restricted to the grain boundaries, giving rise to a local depletion of relatively high intensity. Obviously the latter has the more serious consequences, as discussed later under grain boundary attack.

Increasing carbon content, within the range found in commercial alloys, causes a problem simply through the fact that increasing care need be taken in giving proper heat-treatment, and in this sense carbon may be considered as contracting the passivity range. Metal is not always, in practical use, left in its proper heat-treated condition.

The principal contribution of nickel to the corrosion resistance of 18-8 is to intensify its response to passivating conditions, or in other words to expand the passivity limits. According to Bain⁶: "there is reason to believe that nickel itself possesses to some extent the ability to protect itself with an oxygen layer . . . it may be demonstrated that the restoration of the inert film on a previously stripped nickel-chromium stainless steel is well-nigh instantaneous, vastly more rapid than on the straight chromium alloy. There is the ample explanation for the wider range of industrial applications for the nickel-bearing alloys and for their complete imperviousness in a greater number of environments."

Nickel does have other effects, and positive ones, on corrosion resistance in the case of the higher nickel alloys. Two of these effects will be mentioned here. Nickel itself has a very high resistance to neutral chloride solutions, and to acid solutions of low oxidizing capacity. These are two conditions that for 18-8 lie at the passivity-activity boundary. Thus acid

like sulfuric, if not fairly well aerated, will activate 18-8 and corrode it rapidly. Likewise in brine solutions 18-8 may be activated locally and pitted. Experience has shown that 14 Cr 80 Ni, though possibly not so broad as 18-8 in its passivity range, is far more resistant than 18-8 when the two are in the state of activity. Thus in hydrogen-saturated 5% sulfuric the rate for 14 Cr 80 Ni was 68 mg. per sq. dm. per day. 18-8, on the other hand, in hydrogen-saturated acid gave a rate of 440 mg. per sq. dm. per day. It is well to recall here that the chromium alloys may be at times reasonably satisfactory in use in exposure that may not produce complete passivity and yet that still is remote from a condition of complete activity.

In another example, local activation in sodium chloride solutions has led in a number of cases to very deep, steep-walled progressive pitting of 18-8 under the same conditions where the pitting of 14 Cr 80 Ni has been shallow and not progressive. In fact penetration rates of 18-8 have been eight to ten times greater than for 14 Cr 80 Ni.

The 8% nickel in 18-8 does not accomplish its purpose in one respect—it does not prevent impoverishment of chromium at grain boundaries when the alloy has had to be subjected to heating in the intermediate range of temperature. (See later under grain boundary attack.)

Molybdenum additions are frequently used in 18-8 for its effect in expanding passivity ranges. This is very definitely marked against sulfuric, sulfurous acid at high temperatures and pressures and acids and neutral chloride solutions, including sea water. A good many test results are available as expressions of this fact.^{40, 67, 82, 88}

Two final observations on passivity would seem useful. One has to do with the effect of abrasion on passivity. It has been demonstrated⁴⁰ that 18-8 freshly ground just before immersion and then submerged in a passivating solution requires a number of hours to acquire complete passivity. It was found likewise that in air exposure following grinding twenty-four hours more or less were required to develop complete passivity. The implication is evident that exposure in a solution that is passivating and yet not far removed from the passivity-activity boundary may lead to corrosion if the exposure involves a strong abrasive condition as well. Pitting of pump shafts at packing, handling sea water, may be in some cases accountable to this.

Mention has been made of the pitting that may result beneath adhering substances. The same type of action may result, and has resulted, at minute fractures or pores in the surface of 18-8. Oxidizing capacity is not replenished sufficiently within the pores or cavities to maintain passivity there; once activated the surface surrounding the point is thrown cathodic and penetration within the pore is rapid.

INTERGRANULAR DISINTEGRATION

The intergranular disintegration^{6, 7, 13, 54, 63, 64, 74, 76, 78, 79, 90, 104} of 18-8 has been so much discussed and studied, and mentioned in the technical journals that the simpler facts of its occurrence are often only hazily realized by those who have not had occasion to go into the subject thoroughly.

In the first place 18-8 when properly produced and processed is not susceptible to intergranular attack. The alloy is made susceptible only when held for an appreciable time within the vicinity of 950° to 1400° F. In the progress of welding, a condition of susceptibility develops at the weld and particularly in a zone either side of the weld, where this temperature range has obtained.

The corrosive conditions that may cause grain boundary attack, once the alloy is made sensitive to it by heating in the damaging temperature range, cover those on the border line of passivity-activity to those ordinarily considered fairly safely removed from this. Dilute weak acid solutions, such as carbonic, have been known to embrittle, as well as brines. The standard test for embrittlement susceptibility is immersion in a boiling sulfuric-copper sulfate solution. Such a solution is strongly oxidizing as well as strongly acid. Without the copper the acid would rapidly activate the metal over its entire surface. The copper brings about passivity except at grain boundaries depleted of chromium.

What is the special condition of the metal that makes it susceptible to intergranular attack? There is fairly general agreement as to the specific effect of improper heat-treatment. Bain, Aborn, and Rutherford⁷ describe it as follows:

"The hypothesis which appears to explain both the symptoms and the remedy postulates that the carbon largely dissolved at high temperature and permanently retained in supersaturated solution at ordinary temperatures is rejected in the form of a chromium-rich carbide in the grain boundaries at intermediate temperatures. The formation of such a carbide draws heavily upon the chromium content of the metal adjacent to a carbide particle, thereby impoverishing it in chromium below the concentration required for normal corrosion resistance. Accordingly, a vulnerable pathway through the metal is opened up along grain boundaries wherever fine carbide precipitation occurs."

Solution penetrates along the grain boundary zones and since these alone are in the active condition, all the attack is concentrated on them. It is probable that the remaining passive metal acts cathodically. At any rate the progress of embrittlement may be extremely rapid.

Annealing of 18-8 is accomplished ordinarily by heating at temperatures between 1800° and 2150° F. To prevent carbide precipitation, cooling through the damaging range—950° to 1400° F.—must be rapid.

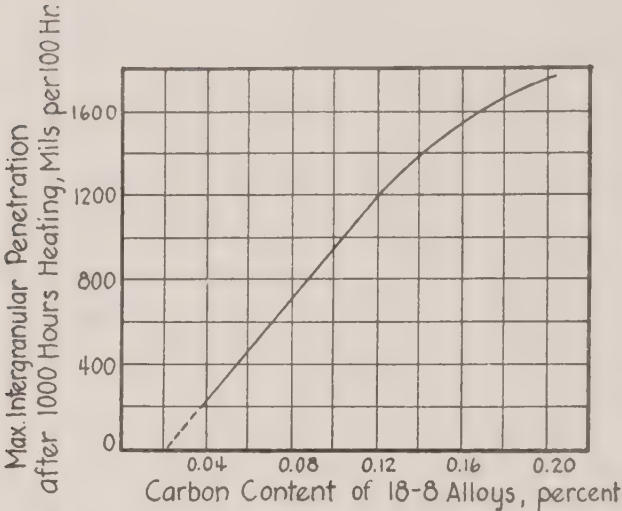


FIGURE 45. Effect of Carbon Content on Sensitivity of 18-8 to Intergranular Attack.⁷

FIGURE 46, (below). Effect of Temperature on Sensitivity of 18-8 to Intergranular Attack.⁷

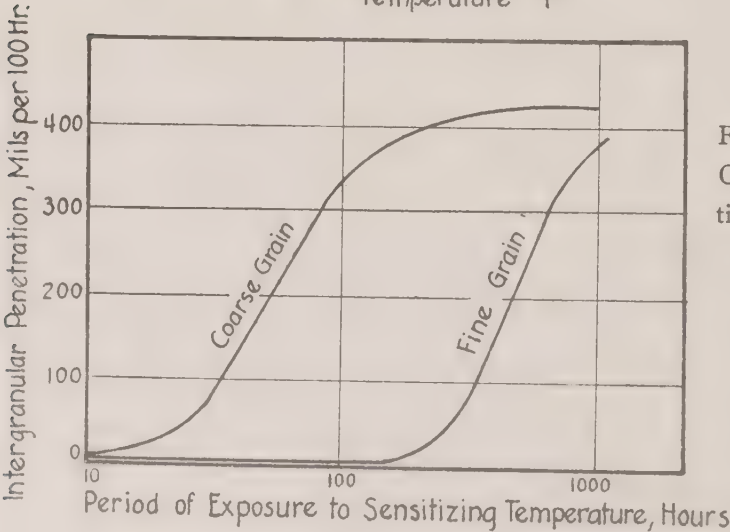
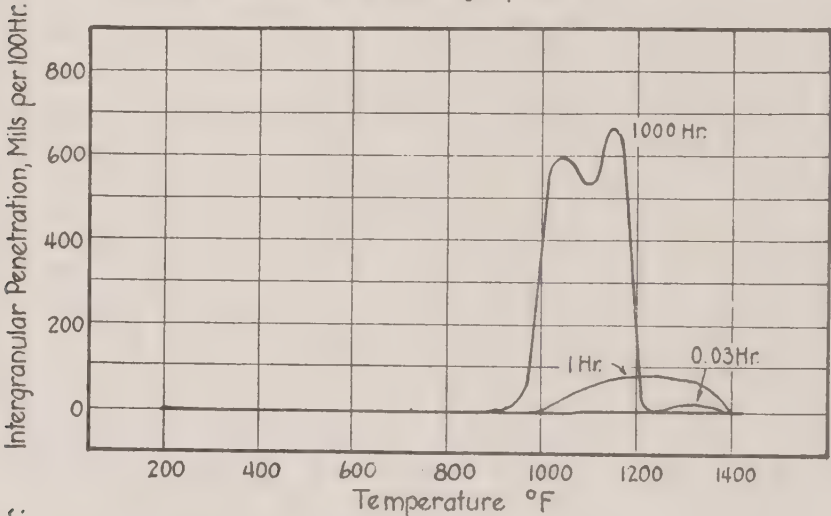


FIGURE 47. Effect of Grain Size on Sensitivity of 18-8 to Intergranular Attack.⁷

Strauss⁷⁸ has mentioned that 0.14 carbon 18-8 cooled from 2100° to 750° F. in four minutes showed a tendency toward intercrystalline embrittlement. Bain, Aborn, and Rutherford⁷ have reported grain-boundary attack on 0.08 carbon 18-8 following two minutes heating in the damaging range; and also that two seconds at 1400° F. will induce precipitation. The heat of welding is a well-recognized sensitizer.

The dependency of susceptibility on carbon content, time, temperature, grain size, is best indicated by the curves in Figures 45, 46 and 47.

Means of avoiding susceptibility to grain-boundary attack have been developed. One method is to make sure that the metal is cooled rapidly through the damaging range, a method used as a natural course in the production of the alloy, following annealing and forging. High temperature treatment and rapid cooling is often also used following welding.

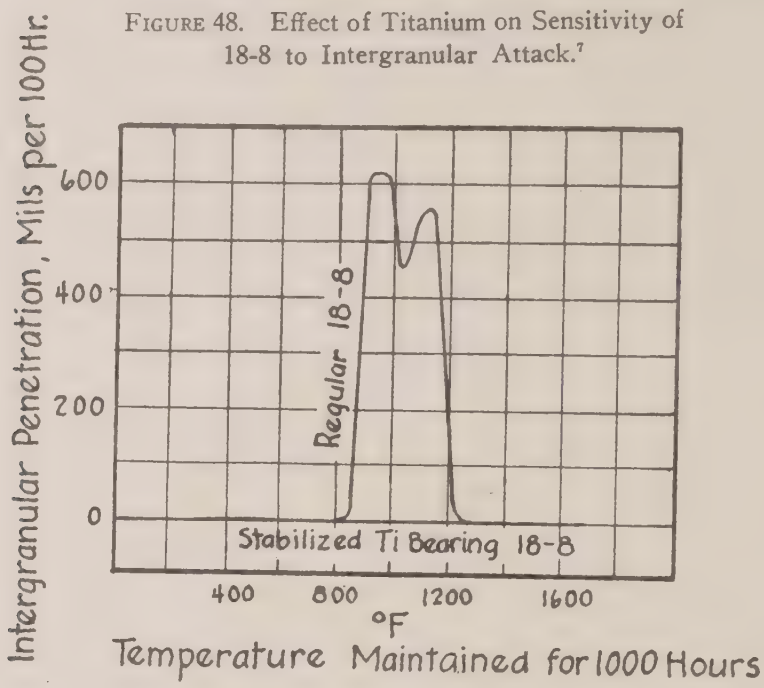
Another method is based on the observation that prolonged heating in the damaging temperature range will in time return the metal to its stable non-susceptible condition. This change is believed to be due to the fact that chromium-impoverished zones become replenished in time by further diffusion of chromium. Complete recovery is a very long-time process, except in the case of cold-worked metal. Bain, Aborn, and Rutherford⁷ have referred to 0.08 C 18-8, 50% cold worked, that at 1100° F. was sensitized to a maximum extent in 2-3 minutes and completely recovered in 10 hours.

Perhaps the most positive means is the addition of carbide-forming elements to 18-8. Titanium has received the most study, though others like columbium are effective. As a stabilizer, titanium acts by taking the place of chromium in the formation of the carbide, with the result that chromium impoverishment does not occur. The curve in Figure 48 best illustrates the comparison between titanium-stabilized and regular 18-8. These investigators have found that a titanium content of about six times the carbon content in excess of 0.02% is a sufficient stabilizer.

Tests⁵⁴ made on welded specimens of low carbon, high carbon, and titanium-stabilized 18-8 in the boiling sulfuric acid-copper sulfate mixture gave the results in Table 163.

TABLE 163.—*Intercrystalline Attack of 18-8.*

Alloy				Penetration in Mils per 500 Hrs.
C	Cr	Ni	Ti	
.07	17.4	9.1		trace
.15	19.6	8.4		120
.07	18.1	9.1	.38	0



TWO-METAL GALVANIC CORROSION

The activity-passivity relationship of the chromium alloys has an important influence on their two-metal galvanic behavior. In the active condition⁸⁷ stainless steels, for instance, are electrochemically not unlike ordinary iron and steel. Given a solution of the type that will produce the active condition and at the same time is a good electrical conductor, the more cathodic metals like copper and copper alloys will accelerate the attack of stainless much as they will steel.

Tests⁴⁰ on 18-8 and Monel metal couples in a nitrogen-saturated 5% sulfuric solution at 86° F.—a non-passivating condition—have given the results in Table 164. The electrodes were of equal area. The 18-8 behaved anodically from the start.

TABLE 164.—18-8 : Monel Couple in Non-oxidizing Acid.

Time from Start Min.	Anode	Current Amperes
0	18-8	.00080
30	18-8	.00083
60	18-8	.00070
90	18-8	.00055
120	18-8	.00055
1170	18-8	.00038
1200	18-8	.00038
1260	18-8	.00038

On the other hand these alloys when passive are extremely stable in galvanic couple even with the copper metals. In fact the 14 Cr 80 Ni alloy in sodium chloride has been found to remain passive, and even to develop passivity following activation with hydrochloric acid, in contact with a much larger area of graphite, a substance noted for its efficiency as a cathode.

In line with these generalizations it is safe, so far as damage to stainless is concerned, to couple it with other metals in exposure to any of the solutions against which it presents its passive surface and against which therefore it is useful. Coupling with other metals will not break down passivity; the damage to the stainless results only when by some other condition of exposure a localized or larger area of the surface becomes active, and at this area two-metal galvanic acceleration takes place.

The effectiveness of stainless as a cathode material is very important to consider in view of the fact that when passive it is strongly cathodic to other metals and therefore potentially able to damage the other metals more or less severely. It has been thought in the past that the protective oxide film on stainless would prevent the steel from being effective as a cathode and therefore that it could be used coupled with iron, for instance, without danger of galvanic attack.

As a matter of fact this belief has proved to be justified in a limited way. In milk,^{57, 101} for instance, stainless will not accelerate corrosion of copper, nickel and the alloys of either, and tin, even though by potential reading the stainless is rather strongly cathodic. Aluminum, iron, and zinc, on the other hand will suffer appreciably when coupled with stainless, yet the degree of galvanic attack on these is considerably less when coupled with stainless than with copper for instance. The following results are typical of those obtained using cathode and anode specimens of equal area (0.5 sq. dm) in quiet immersion in sweet milk at 149° F.⁵⁷:

18-8 coupled with nickel — <.01 milliampere.

Copper coupled with nickel—1.9 to 0.62 milliamperes.

18-8 coupled with aluminum — .17 to .10 milliampere.

Copper coupled with aluminum — 8 to .90 milliamperes.

It must be kept in mind, however, that milk is quite individual in bringing about this low degree of effectiveness of stainless as a cathode. In sea water,¹⁸⁻²² sodium sulfate and sulfurous acid,¹⁰⁰ concentrated sodium chloride solutions and acetic acid⁴⁰ stainless has behaved like any other cathode material in causing galvanic attack on the other metal of the couple. These solutions are typical of those to which stainless normally offers its passive surface. At times, it is true, stainless has been somewhat less effective than other cathodes, yet at others more effective. These variations therefore are not due to a specific property

of the metals but rather to the metals-exposure relation. There is a suggestion¹⁰⁰ that stainless as a cathode is more effective when depolarization is due to oxidizers rather than hydrogen evolution.

Tests have been made¹⁰⁰ on iron coupled with 18-8 and platinum respectively in fully aerated, agitated 3.5% sodium sulfate at 86° F. The area of iron (.142 sq. dm.), anodic in both couples, was slightly over one-half the area of the cathode. The results were as given in Table 165.

TABLE 165.—Iron Couples vs. Aerated Salt Solution.

	Corrosion of Iron—Mg.	
	18-8 vs. Iron	Platinum vs. Iron
Total corrosion	102.6	107.4
Uncoupled corrosion	37.4	36.9
Galvanic corrosion	65.2	70.5

Aerated, agitated 5% sulfuric acid at 86° F. gave the results in Table 166, with Monel metal specimens anodic. The anode area was .15 sq. dm., the cathode .26 sq. dm.

TABLE 166.—Monel Couples vs. Aerated Acid.

	Corrosion of Monel—Mg.	
	18-8 vs. Monel	Platinum vs. Monel
Total corrosion	42.4	49.1
Uncoupled corrosion	33.7	34.2
Galvanic corrosion	8.7	14.9

In a saturated impure solution of sulfur dioxide at 122° F., the data in Table 167 were obtained in aerated, agitated exposure of 20 hours. The bronze was anodic.

TABLE 167.—Bronze Couples vs. Sulfurous Acid.

	Corrosion of Bronze—Mg.	
	Valve Bronze vs. 18-8	Valve Bronze vs. Platinum
Anode area .	0.153 sq. dm.	0.154 sq. dm.
Cathode area	0.430 sq. dm	0.413 sq. dm.
Total corrosion	52.5	48.1
Uncoupled corrosion	8.8	8.8
Galvanic corrosion	43.7	39.3

Tests⁴⁰ in saturated sodium chloride-solution, aerated and agitated, at 185° F. have given the results in Table 168.

TABLE 168.—Cast Iron Couples vs. Aerated, Hot Salt Solution.

	Corrosion of Cast Iron—Mg.	
	Monel Cathode	18-8 Cathode
Anode area .	0.15 sq. dm.	0.15 sq. dm.
Cathode area	0.35 sq. dm.	0.35 sq. dm.
Total corrosion	79.9	101.7
Uncoupled corrosion	33.0	33.0
Galvanic corrosion	46.9	68.7

Another interesting and important observation has been made on the two-metal galvanic behavior of chromium alloys.¹⁰⁰ This is that an alloy activated before being placed in coupled immersion in a solution which normally passivates it, is still able to develop passivity on immersion. Thus the development of passivity is indicated in the data in Table 169 on a couple consisting of freshly ground 18-8 and Monel metal, in fully aerated, agitated 5% sulfuric at 86° F. The Monel area was 0.15 sq. dm., the 18-8 area .270 sq. dm.:

TABLE 169.—18-8:Monel vs. Aerated Acid.

Time from Start Min.	Anode	Current amperes
0	18-8	.0060
30	18-8	.0038
60	18-8	.0031
1020	Monel	.00012
1140	Monel	.00012

Hydrogen deposition at an 18-8 cathode does not destroy its passivity in simple galvanic couples, as current and potential measurements made in connection with the tests described above have shown. It is true, however, the strong evolution of hydrogen that results from an impressed current on a stainless cathode does destroy passivity.^{62, 100}

ACIDS

The effect of acids on the chromium alloys is dependent on whether the oxidizing capacity or the acidity of the solution gains the upper hand. In one case, as strong nitric, the alloys are thoroughly passive, with rates ranging below 1 mg. per sq. dm. per day. Strong nitric is very powerfully oxidizing and rather mild in hydrogen-ion concentration. In strong hydrochloric, on the other hand, acidity dominates the very mild oxidizing capacity of dissolved oxygen. Consequently corrosion is rapid.

The boundary between conditions that maintain passivity and those that produce corrosion is often a fairly definite one. Results in sulfuric acid bring this out clearly. A 3% sulfuric acid solution through which hydrogen was bubbling has corroded 18-8 at a rate of over 400 mg. per sq. dm. per day which is rapid when viewed commercially. The same solution with oxygen rather than hydrogen bubbling through it gave a rate of 4 mg. per sq. dm. per day—a passive condition.

Of course acid solutions are not frequently encountered that have either oxygen or hydrogen bubbling through them, but the comparison is useful as an illustration of the importance of oxidizing capacity, or rather the struggle between oxidizing capacity and acidity. Most acid solutions handled at room temperature carry a moderate concentration of dissolved

oxygen absorbed from the air. This is sufficient to produce passivity in most solutions that have not a very high hydrogen-ion concentration.

Acting with oxidizing capacity and acid strength are a number of other factors that determine the passivity-activity boundary. These are chromium content, nickel content, and carbon content, and heat treatment. All these factors are dependent on each other in their influence and it is for this reason that the boundary is not always readily anticipated. It is possible, however, to outline fairly accurately the behavior of 18-8 stainless steel that has been properly heat-treated (i. e. that has not been held between 950° and 1400° F. for an appreciable length of time):

1. Acid solutions of high hydrogen-ion concentration are resisted only if the oxidizing capacity of the solution is strong. Nitric of 1 to 15% concentration is an example of an acid that has sufficiently high oxidizing capacity to take care of the high hydrogen-ion concentration. Sulfuric acid of 1 to 15% concentration when strongly aerated produces passivity but if not strongly aerated is corrosive. Hydrochloric acid of 1% or higher even though strongly aerated is not resisted.

2. Acid solutions of intermediate hydrogen-ion concentration are well resisted so long as the oxidizing capacity is moderate. The dissolved oxygen normally present in a solution, quiet or in motion, that is freely exposed to the air is often sufficient for passivity in such solutions as sulfuric, tartaric, formic, phosphoric, of 0.1% concentration and less, or acetic of any concentration. On the other hand these solutions in the absence of dissolved air or when carrying reducing agents, are likely to be corrosive. In this class also are strong sulfuric and nitric solutions (e. g. over 30%), which are not high in hydrogen-ion concentration.

3. Hydrochloric acid differs somewhat from the other acids in that passivity is more difficult to produce. In fact though there have been cases of passivity in hydrochloric this is the unusual condition even in very low concentrations of hydrochloric.

4. Oxidizers like ferric and cupric salts, in acid solutions, are more favorable to passivity than dissolved oxygen. The presence of these in sulfuric solutions is particularly beneficial.

5. Oxidizing capacity, when insufficient to maintain passivity, is an accelerant of corrosion. It is important to note that under conditions at the active-passive boundary corrosion may be extremely active or almost completely absent, depending on whether the passivating effect of the oxidizing capacity has the upper hand or not.

6. Pitting attack is a result of localized activity on a passive surface. The presence of chlorides and other halides in acids frequently leads to pitting. Generally speaking, however, the conditions that cause pitting are not clearly apparent.

7. Elevated temperatures shift the active-passive border line in such a direction that a good many of the conditions that produce passivity at room temperature cause rapid corrosion at elevated temperatures. An important reason for this is the lowering of dissolved oxygen content by rising temperatures. Passivity is maintained in hot nitric because the oxidizing capacity of the solution is not altered by the temperature rise. Boiling solutions of sulfuric, tartaric, phosphoric, formic, etc., may be on the other hand extremely corrosive.

Nitric acid. Nitric acid ^{9, 28, 56, 60, 65, 67, 77, 82} solutions, very strongly oxidizing, are widely handled by the chromium alloys. The chromium in the alloys is principally responsible for their resistance, nickel contributing

in a minor way. Typical corrosion rates are 10 mg. per sq. dm. per day and less. Corrosion has a tendency to be greater in the more dilute—1 to 20%—range, but with chromium contents of 18% and greater even these concentrations are ordinarily well resisted. With 13 to 14% chromium, whether straight chrome iron or with up to 80% nickel, rates in 1 to 20% acid range up around 300 to 400 mg. per sq. dm. per day. Yet in 25-30% acid and higher rates for these are 10 mg. per sq. dm. per day and less.

Pilling and Ackerman⁶⁵ have made tests in nitric on a large number of Cr Ni Fe compositions. Their results are unusual in that the rates are far higher than rates reported by other investigators. Prior heat-treatment consisted of a 30-minute anneal at 1832° F. followed by furnace cooling, which is a heat-treatment that is not favorable to corrosion resistance. The tests were run in thoroughly aerated agitated 5% and 35% solutions at 86° F. In the dilute acid the rates even of 28-32 Cr were high enough (1-hour exposure) to be considered on the active side of the boundary. In 35% acid (54 min., 2.5 hours, 20 hours) passivity was well developed with 10 Cr and greater, both with and without nickel, rates ranging from 85 to 1 mg. per sq. dm. per day, and less.

Boiling acid in the case of the 14% chromium alloys is much more corrosive in the 1 to 20% acid range, but in the higher concentrations boiling acid is often no more corrosive than acid at room temperature. With 18% chromium and greater, rates in boiling acid range below 100 mg. per sq. dm. per day, and usually much below this.

Tons of chromium alloys are used for equipment in the manufacture of nitric acid from atmospheric nitrogen, where the concentrations of nitric run 55 to 65%. On the other hand nitric carrying chlorides or other halides, characteristically present in acid made from saltpeter, is corrosive to the chromium alloys, the halides preventing passivity.

Hydrochloric acid. As a rule one of the strongest reactants with chromium alloys, even hydrochloric exposure at times has produced the passive condition, with rates as low as 1 mg. per sq. dm. per day at room temperature. Molybdenum makes a very marked contribution to resistance, as noted in Table 170.⁶⁷

TABLE 170.—24 Cr 10 Ni vs. Hydrochloric Acid.

Corrosion Rate—Mg. per sq. dm. per day				
	24 Cr 10 Ni	Molybdenum Addition	Tungsten Addition	Silicon Addition
1500 hrs., 77°-86° F.				
1% conc.	19			3
2% "				21
5% "			<1	
10% "		<1	29	
15% "		<1	89	
20% "		400		

Passivity was likewise in evidence in boiling acid, over a 300-hour period. See Table 171.

TABLE 171.—24 Cr 10 Ni vs. Boiling Hydrochloric Acid.

Corrosion Rate—Mg. per sq. dm. per day				
Boiling	24 Cr 10 Ni	Molybdenum Addition	Tungsten Addition	Silicon Addition
0.1% conc.	<1			<1
0.2% "	960			1400
0.5% "			<1	
1.0% "		<1	1400	
1.5% "		<1		
2.0% "		<1		
2.5% "		<1		

The extremely interesting results in Table 172 were also obtained—interesting in that they show the progress of passivity. The alloy was the 24 Cr 10 Ni with molybdenum, and the acid boiling 1% hydrochloric. The same specimen was reimmersed three times.

TABLE 172.—24 Cr 10 Ni, + Mo, vs. Boiling Hydrochloric Acid.

	Corrosion Rate Mg. per sq. dm. per day
First period, of 22 hrs.	33
Second period, of 21 hrs.	9
Third period, of 32 hrs.	2
Fourth period of 575 hrs.	<1

Other investigators ⁶⁵ found that thoroughly aerated, agitated 5% hydrochloric failed to produce passivity on Cr and Cr Ni Fe alloys up to 32 Cr. The lowest rates, 700 to 1000 mg. per sq. dm. per day, applied to those carrying 13 Ni and greater, regardless of the chromium content. Pre-treatment of these alloys consisted of 30-minutes anneal at 1832° F. followed by furnace cooling, which is unfavorable to resistance.

Still other data ^{40, 48, 60, 77, 82} indicate decided activity for hydrochloric solutions.

Sulfuric acid. Sulfuric acid ^{1, 28, 41, 43, 65, 67, 68, 77, 82, 88, 89, 103} is very clearly a passivity-activity border line condition. In one set of tests ⁶⁵ in thoroughly aerated, agitated 5% acid passivity failed to develop on alloys ranging up to 32% chromium, both with and without nickel; the preheat-treatment was such as to militate against passivity.

In another set ⁶⁷ on 24 Cr 10 Ni, all concentrations produced passivity, in 1500 hour exposure of unstated aeration degree, at room temperature. The rates were less than 1 mg. per sq. dm. per day. In boiling acid the passivity limits, in these tests, are indicated by the data on page 286.

Oxidizing capacity, if strong enough, will give passivity even in solutions of high hydrogen-ion concentration. Thus in 1 and 3% acid saturated with

oxygen the rates were 2 to 4 mg. per sq. dm. per day, whereas in hydrogen-saturated solution the rate in 1% acid was 96 and in 3% 440 mg. per sq. dm. per day.⁴⁰

It does seem true however, that concentrated (80 to 100%) acid is very well resisted by 18-8, with rates as low as 1 to 2 mg. per sq. dm. per day at room temperature. The rates go up rapidly with temperature rise, however.

Strong oxidizers in sulfuric very notably enlarge the passivity range of the stainless steels. Copper sulfate, ferric sulfate, nitric acid have such an effect. With these mixtures the metals are usually resistant.

In nitric-sulfuric mixtures 18-8 is passive at room temperature. A 58/40/2 sulfuric/nitric/water mixture gave the following:⁸²

68° F.	<2 mg. per sq. dm. per day
140° F.	12 mg. per sq. dm. per day
212° F.	170 mg. per sq. dm. per day
230° F.	1800 mg. per sq. dm. per day

Strauss^{88, 89} in various mixtures at the boiling point obtained rates of 150 to 2000 mg. per sq. dm. per day. Other tests¹ gave rates of 350 to 116,000 mg. per sq. dm. per day for 18-8 in boiling mixtures. Still others⁶⁷ gave 20 to 100 mg. per sq. dm. per day in acid mixtures at 212° F. to boiling for 24 Cr 10 Ni, with additions of molybdenum or tungsten to this alloy giving some what better performance.

These results therefore indicate that boiling mixtures are critical in the sense that they may or may not be very corrosive to the 18-8 and related alloys. Below the boiling point these alloys are well resistant.

Copper or ferric sulfate in sulfuric solutions exerts a strong passivating effect. As an example, the rates in Table 173 were obtained⁶⁰ in a 10% sulfuric solution on a 12.6 Cr 0.3 C steel, hardened and tempered:

TABLE 173.—*Cr Fe vs. Oxidizing Acid.*

Conc. of Ferric Sulfate Grams per liter	Duration	Corrosion Rate Mg. per sq. dm. per day
0	24 hours	1300
5	"	1500
10	"	1600
15	"	1700
20	36 days	<24
40	"	<24
60	"	<24

Boiling copper sulfate and sulfuric mixtures are used as a rapid test for susceptibility to grain boundary attack of 18-8. Suitably annealed low carbon 18-8 remains unchanged in a boiling 10% sulfuric and 10% copper sulfate solution, yet the alloy that has been given a damaging heat treatment is very actively penetrated along grain boundaries within a period up to

several hundred hours. At room temperatures, 18-8 is thoroughly resistant to copper sulfate and sulfuric mixtures.

Tests on chromium iron alloys gave the results ⁶⁰ in Table 174, which are particularly valuable in indicating where the boundary between active and passive states lies in 25% sulfuric at room temperature.

TABLE 174.—Cr Fe vs. Sulfuric: Copper Sulfate Solution.

Copper Sulfate	12 Cr .09 C	13 Cr .14 C	14 Cr .09 C	17.5 Cr .13 C
4%	passive	passive	passive	passive
3%	"	"	"	"
2%	active	"	"	"
1%	"	"	"	"
0.5%	"	active	"	"
0.25%	"	"	active	"
0.125%	"	"	"	"

Other oxidizing agents are passivating in a manner similar to copper and ferric sulfate. Tests ⁶⁸ on silver sulfate, mercurous sulfate and potassium ferri-cyanide gave the following results:

	Mg. per sq. dm. per day
Boiling 20% sulfuric	
0.1% silver sulfate	16
0.1% mercurous sulfate	9
0.1% copper sulfate	7.5
Boiling 5 (by volume) sulfuric (66° Bé)	
0.1% ferric sulfate	<1
0.1% potassium ferricyanide	4
No added salt	43,000

Sulfurous acid. Passivity is characteristic of the chromium alloys in sulfurous acid ^{11, 13, 14, 26, 54, 65, 80, 82, 92} provided the alloy content is sufficient. When active the alloys are rapidly attacked, either with dissolution or with intercrystalline attack. Chromium of course confers the passivity, alloys with under 12 to 15% chromium being attacked seriously in solutions even at ordinary temperature, and the higher chromium alloys being passive. Nickel is beneficial in somewhat lowering the chromium necessary to confer passivity.

An excellent survey of the action of pure sulfurous on chromium alloys is given by Figure 49.⁶⁵ The alloys were given a 30 min. anneal at 1832° F. followed by furnace cooling, a treatment favoring corrosion.

A rate of 1 mg. per sq. dm. per 54 min. corresponds to 26 mg. per sq. dm. per day. Attention is called to the tremendous difference between active and passive metal in rate of attack.

Commercially, chromium-nickel-iron is widely and very successfully used in equipment handling the impure sulfurous acid solutions of sulfite digestors, in the paper industry. 18-8 and the higher alloys, either wrought or cast, when properly made have almost unlimited life. Several papers

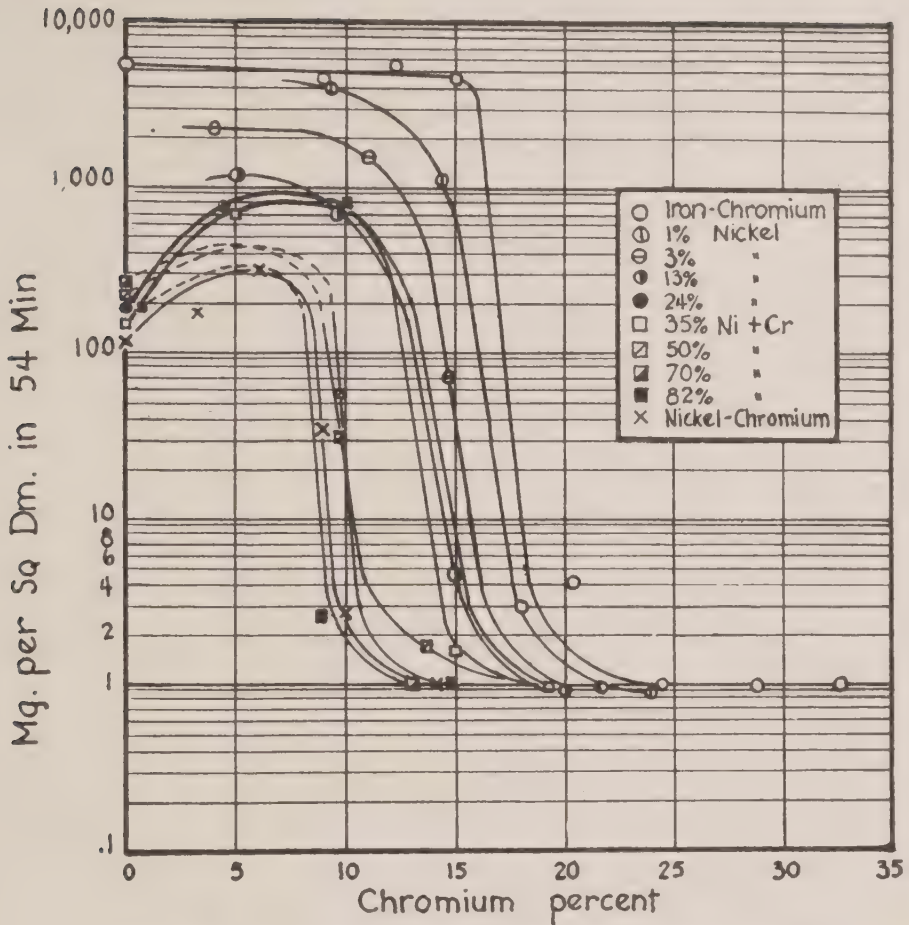


FIGURE 49. Chromium Alloys vs. Pure 5% Sulfurous Acid.⁶⁵

¹³, ⁵², ⁹² have mentioned the rapid intergranular failures of some compositions associated with carbide precipitation, due either to insufficient alloy or to improper heat-treatment. These sulfite liquors seem to constitute a milder grain-boundary-attacking condition than the boiling sulfuric-copper sulfate solution often used in testing for susceptibility. Yet the conclusion has been drawn ⁵⁴ that it is desirable to take special precautions in using low carbon 18-8 or titanium-stabilized 18-8, if welding without subsequent heat treatment is employed, and, in the case of castings, high temperature, rapid-cooling treatment.¹³

Molybdenum is desirable in handling extremely hot saturated sulfurous.² See Table 175.

The presence of sulfuric acid or chloride in sulfurous tends to contract the passivity limits. Pilling and Ackerman ⁶⁵ have observed that a stale solution of sulfurous has stained 15 Cr 15 Ni vigorously, a composition "normally passive by a good margin." This effect was traced to a small

TABLE 175.—18-8 vs. Sulfurous Acid.
Corrosion rate—Mg. per sq. dm. per day

° F.	Pressure Lbs.	18-8	18-8 Mo
68	Atmos.	<24	<24
272	60	<24	<24
320	70-125	240-720	<24
356	150	240-720	<24
392	200	240-720	24-240
392	300	240-720	24-240

content of sulfuric in the acid. They state also "a steel containing 28% Cr suffered no detectible corrosion in pure 5% sulfurous; the addition of 5% NaCl, which in itself is also without effect on this steel, brought about a corrosion rate of 95,000 mg. per sq. dm. per day, as great as that of dilute hydrochloric acid."

Phosphoric acid. Phosphoric solutions,^{45, 65, 67, 69, 76} behave with great complexity. Pilling and Ackerman⁶⁵ have reported activity for 15 Cr, 15 Cr 13 Ni, 15 Cr 20 Ni, that had been given a damaging heat-treatment, in 5% thoroughly aerated, agitated phosphoric at 86° F.

An interesting series of tests made by Portevin and Sanfourche⁶⁹ have indicated the behavior of Cr Ni Fe. Three solutions were used: 1. 75% concentration derived from burning phosphorus, 2. This solution diluted to 40%, 3. A 40% solution derived from superphosphate. Impurities in solutions 1 and 2 consisted of very small quantities of acids of phosphorus of lower degrees of oxidation; solution 3 carried sulfuric acid, salts of iron, aluminum, chromium, magnesium and calcium, and also fluorine compounds, as impurities. The tests were made in the quiet solutions at 59° to 62° F., over exposure periods up to 250 hours.

In all three solutions only one alloy, 21 Cr 8 Ni, remained passive to the end of the test, with rates under 1 mg. per sq. dm. per day. In the dilute and concentrated pure acid 13 Cr remained passive and in the dilute 11 Cr and 10 Cr 23 Ni remained passive. In the concentrated pure acid 12 Cr 32 Ni, 11 Cr 52 Ni, and 10 Cr 23 Ni had rates of about 25 mg. per sq. dm. per day, and in the dilute pure acid 12 Cr 32 Ni had a rate of 80 mg. per sq. dm. per day, which would seem to be the minimum rate for chromium alloys in their active state, under these exposure conditions. In the impure solution the active alloys gave rates ranging above 400 mg. per sq. dm. per day.

In another set of results⁶⁷ it is reported that 24 Cr 10 Ni gave rates of less than 1 mg. per sq. dm. per day at 86° F. This was true of alloys with the same ratio of chromium and nickel but with a few per cent molybdenum, tungsten, and silicon respectively. In hot acid the rates in Table 176 were obtained:

TABLE 176.—24 Cr 10 Ni vs. Hot Phosphoric Acid.

Corrosion rate—Mg. per sq. dm. per day				
	24 Cr 10 Ni	Tungsten Addition	Molybdenum Addition	Silicon Addition
Boiling				
20% conc.				5
25% conc.				960
50% conc.	8		7	
55% conc.	96		700	
At 212° F.				
65% conc.	4	9	28	3700
80% conc.	12			
At 176° F.				
80% conc.	<1			

Obviously the resistance of chromium alloys to phosphoric acid is extremely sensitive to some unknown factors. Other results,^{40, 60, 82} confirm this. Based on indirect evidence it may be said that the presence of ferric iron tends strongly to make the alloys passive, and the presence of chlorides or other halides and of reducing agents (possibly phosphorus in intermediate degree of oxidation) to make them active.

According to report a good many tons of stainless have been used in the construction of phosphoric manufacturing plants.

Hydrogen sulfide. Chromium alloys are normally excellent against hydrogen sulfide and water mixtures at ordinary temperature. Unlike nickel and copper, these alloys do not even tarnish, in exposure at room and slightly elevated temperatures. Johnson⁴¹ has given a rate of 350 mg. per sq. dm. per day for a 27% chromium iron in a boiling saturated solution of hydrogen sulfide. This would indicate that there is a temperature limit to the passive range of the chromium alloys. Just where it lies is problematical. On the other hand he records a rate of 28 mg. per sq. dm. per day for 8 Cr 24 Ni 3 Si in hydrogen sulfide at 194-212° F., and less than 1 mg. per sq. dm. per day for stainless iron. In another test⁴⁰ alloys were exposed in an atmosphere of hydrogen sulfide, air, and moisture at 150° F. 18-8 gave a rate of 175 and 14 Cr 80 Ni a rate of 58 mg. per sq. dm. per day.

Chromic acid. The chromium alloys are normally passive in chromic acid. The acid is a strongly oxidizing one and yet not strongly ionizing. Chromic in the presence of stronger, non-oxidizing acids that are hot enough to make the alloys active is strongly accelerating on corrosion. Thus in the case of 14 Cr 80 Ni a 70% boiling acetic solution gave a rate of 80 mg. per sq. dm. per day. The addition of 0.1% potassium dichromate led to rates of 150 to 2000 mg. per sq. dm. per day.⁴⁰ In other tests⁴⁰ 18-8 partially immersed in a fractionating still handling concentrated acetic with a small sodium dichromate addition at 240° F. for 387 hours was

corroded at rates of 25 to 60 mg. per sq. dm. per day. Undoubtedly in this case the dichromate acted in its passivity-producing capacity, as contrasted with its strongly accelerating effect in the former test.

Acetic acid. Chromium-nickel-iron is characteristically passive in acetic acid solutions ^{2, 40, 41, 43, 50, 59, 60, 65, 67, 82, 88} of all concentrations at room temperature, with rates ranging 1-2 mg. per sq. dm. per day and less. This is true of 18-8 and its modifications as well as of alloys higher in nickel. The simple chromium alloys, though having a tendency to be passive, are more likely to corrode, rates running from 25 to 2500 mg. per sq. dm. per day. In a set of tests in air-saturated, agitated acid solutions rates for a low carbon 14% chromium stainless ranged from 500 mg. per sq. dm. per day in 1% acid to 2500 in 100% acid.

Against thoroughly aerated, agitated 5% acetic at 86° F., Pilling and Ackerman ⁶⁵ found three 15 Cr compositions (0, 13, 20 Ni respectively) to be active, with rates over 200 mg. per sq. dm. per day. These alloys had had a damaging heat treatment.

In hot acid the austenitic nickel-bearing stainless group still have a tendency to be passive, though less certainly so than at ordinary temperatures. A number of tests in hot and boiling acid of all concentrations by different investigators has yielded rates of 80 mg. per sq. dm. per day and less, several rates running under 10 mg. per sq. dm. per day. On the other hand, rates occasionally have run above 200 to a maximum for 18-8 of 2400 mg. per sq. dm. per day in boiling 80% acid. In hot acid the 14% chromium steels are likely to be strongly attacked.

Glacial acid seems to behave much like the aqueous solutions, some tests indicating passivity, others activity. Boiling mixtures of glacial acetic and anhydrous acetic have corroded 18-8 at rates of 100 to 400 mg. per sq. dm. per day, specimens exposed in the vapor being less attacked than those in the liquid. ⁴⁰

Molybdenum has been found beneficial in 24 Cr 10 Ni alloy, ⁶⁷ as indicated in Table 177 for boiling acid.

TABLE 177.—24 Cr 11 Ni vs. Boiling Acetic Acid.

Conc.	Mg. per sq. dm. per day	
	24 Cr 11 Ni	With 4.4% Molybdenum
40%	<1	<1
80%	31	<1
Glacial	72	<1
Anhydrous (140° F.)	—	<1
Anhydrous	140	72

Monypenny ⁵⁹ also found molybdenum beneficial in 17-18 Cr 10 Ni; with 3.42 Mo, in boiling acid of 5, 10, 15 and 33% the alloy was passive, whereas without the molybdenum passivity broke down in the 15 and 33%

acid. 20.9 Cr 10.6 Ni 3.78 Mo alloy was passive in acid from 5 to 100% concentration. Passivity of 15 Cr broke down in moderate concentrations at room temperature, of 20.7 Cr in moderate concentrations at 176° F. and boiling, and of 18-8 only in boiling.

Other organic acids. In general, the behavior of the alloys in acetic acid is typical of behavior in other organic acids—formic, tartaric, citric, lactic, malic, oxalic, etc. At room temperatures in quiet or agitated exposure, 18-8 remains passive as a rule. Boiling solutions of the high hydrogen ion range generally, though not always, produce activity, and of the weaker hydrogen ion range passivity. The 14% chromium alloys without nickel are sometimes active, sometimes passive at room temperature, but active before the boiling point is reached. The high (27%) chromium irons are passive at room temperature, active at boiling temperatures, except in the case of weak acid solutions.

In Table 178 are given the results of tests made by a number of investigators. Rates under passivating conditions ran less than 10 mg. per sq. dm. per day, in the active condition over 100 mg. per sq. dm. per day and usually much above this.

TABLE 178.—Cr Ni Fe vs. Acid Solutions.

		Active	Passive
<i>Reference 82</i>			
Oxalic conc.,	68° F.		20 Cr 7 Ni
	104° F.		20 Cr 7 Ni
	boiling	20 Cr 7 Ni	
Oleic,	302° F.		20 Cr 7 Ni
Butyric,	68° F.		20 Cr 7 Ni
	266° F.		20 Cr 7 Ni
Formic, 10%	boiling	20 Cr 7 Ni	
	50% boiling	20 Cr 7 Ni	
Lactic,	68° F.		20 Cr 7 Ni
Carbolic, crude	194° F.		20 Cr 7 Ni
Citric, 5%	boiling		20 Cr 7 Ni
	boiling	20 Cr 7 Ni	
Gallic, sat'd,	boiling		20 Cr 7 Ni
Tartaric, sat'd,	boiling	20 Cr 7 Ni	
<hr/>			
<i>Reference 40</i>			
Formic, 90%, submerged, 212° F.			18-8 (low C)
			18-8 (high C)
			18-8 (Mo)
			18-8 (Ti)
90%, in hot vapor		18-8 (low C)	
		18-8 (high C)	
		18-8 (Ti)	
90%, submerged, room			18-8 (all)
	part. imm., room		18-8 (all)
Lactic, 30% impure, 80-150° F. concen-			
trating from 5 to 48% vacuum			18-8 (all)
Fatty acids, crude split, 440° F.			
	vapor		18-8 (pitted)
	liquid		18-8

Reference 37

Partial immersion, room temp.		
Acetic, 1% } Lactic, 1% } Butyric, 1% } Citric, 0.2% }	{ 18-8 14 Cr 17 Cr
Partial immersion, 145° F.		
Butyric, 1% } Lactic, 1% }	{ 18-8 14 Cr 17 Cr

Reference 43

Monochloroacetic,	room	20 Cr 65 Ni
	212° F.	20 Cr 65 Ni
Trichloroacetic, 50%,	room	20 Cr 65 Ni
	212° F.	20 Cr 65 Ni

Reference 65

5% acid, fully aerated, room		
Citric	15Cr, 15Cr12Ni, 15Cr20Ni*	
Formic	15Cr, 15Cr12Ni, 15Cr20Ni*	
Lactic	15Cr, 15Cr12Ni, 15Cr20Ni*	
Oxalic	15Cr, 15Cr12Ni, 15Cr20Ni*	
Tartaric	15Cr, 15Cr12Ni, 15Cr20Ni*	
Acetic	15Cr, 15Cr12Ni, 15Cr20Ni*	
Benzoic		15Cr, 15Cr12Ni, 15Cr20Ni*
Carbolic		15Cr, 15Cr12Ni, 15Cr20Ni*

* These alloys had had a damaging heat treatment.

Reference 41

Formic, 85%	room		27 Cr
	200° F.	27 Cr	
Lactic, 25%	200° F.	27 Cr	
Citric, moderate conc.	212° F.		27 Cr
Gallic, 25%	212° F.		27 Cr

The 14 Cr 80 Ni composition,⁴⁹ though having a more confined range of passivity than the 18-8 alloy, is, because of its high nickel content, much less corroded when in the active state than 18-8. A number of rates are given in Table 179.

TABLE 179.—14 Cr 80 Ni vs. Acids.

		Mg. per sq. dm. per day
Formic, 90%, 212° F.,	submerged	110
	vapor	72
room,	submerged	22
	part. imm.	33
Lactic, 30% impure, 80–150° F.	4
concentrating from 5 to 48%, under vacuum	21
Fatty acid, crude split, 440° F.		
	vapor	5
	liquid	6.4

CAUSTIC ALKALIES

Caustic potash or soda solutions of any concentration at room temperature are well resisted by ordinary iron and steel, and likewise by stainless. Elevated temperature, however, may be much more accelerating for chromium alloys than for straight iron. With elevated temperatures the resistance of stainless continues to be good at moderately high concentrations and temperatures. With further increase in temperature or concentration the uncertain zone is entered where either passivity or activity may result. Where active, the alloys are corroded at much higher rates than ordinary steels.

The data in Table 180 give a fair idea of behavior of the chromium alloys in hot caustic.

TABLE 180.—*Chromium Alloys vs. Caustic Solutions.*

Condition				Alloy	Mg. per sq. dm. per day
<i>Reference 40</i>					
NaOH,	70%,	260° F.	720 hrs.	18 Cr 8 Ni	2
NaOH,	23%,	220° F.	720 hrs.	18 Cr 8 Ni	<1
NaOH,	10%,	170° F.	720 hrs.	18 Cr 8 Ni	<1
<i>Reference 67</i>					
KOH,	55%,	boiling,	100 hrs.	24 Cr 10 Ni	41
NaOH,	30%,	176° F.	24 Cr 10 Ni	9
	30%,	boiling,	24 Cr 10 Ni	31
Na ₂ CO ₃ ,	25%,	boiling,	24 Cr 10 Ni	<1
<i>Reference 82</i>					
NaOH,	20%,	230° F.	20 Cr 7 Ni	5
	34%,	212° F.	20 Cr 7 Ni	<2
KOH,	27%,	boiling.	20 Cr 7 Ni	<2
	50%,	boiling,	20 Cr 7 Ni	96
<i>Reference 83</i>					
NaOH, 30-50%, 179° F. 380 hrs.				Steel	20
				Cast Iron	35
				14 Cr Fe	180
				18-8	1,700
NaOH, concentrating from 75% to anhydrous, rod specimens rotated at high speeds; air present				18-8	9,890
				18.5 Cr	15,050
				20 Cr 80 Ni	550

The last set of data suggests the extreme corrosiveness of very high concentrations of hot caustic and the beneficial effects of high nickel content. Tests on fused caustic ⁸² have given the results in Table 181.

TABLE 181.—*20 Cr 7 Ni vs. Fused Caustic.*

Condition				Alloy	Mg. per sq. dm. per day
NaOH,	fused,	600° F.	20 Cr 7 Ni	53
KOH,	fused,	680° F.	20 Cr 7 Ni	840
	fused,	1112° F.	20 Cr 7 Ni	8,900

AMMONIA SOLUTIONS

Iron and steel are widely used for handling ammonia solutions.^{46, 60, 79, 87} The chromium alloys are virtually completely resistant, and furthermore have the advantage over steel of not rusting under moist neutral conditions. Corrosion rates for the 18-8 alloy and other high chromium alloys may be taken at less than 1 mg. per sq. dm. per day.

SALT SOLUTIONS

Resistance of the chromium alloys to salt solutions depends largely on the efficiency of the protective oxide film. Salt solutions usually carry sufficient dissolved air to maintain this film. Certain qualifications are necessary, however. Chloride salts present a problem not met with non-chloride salts. It should be said at this point that generally speaking solutions of the non-chloride salts are well handled by 18-8 and by the austenitic alloys of lower chromium content. The 14 Cr 80 Ni type of alloy is likewise in the group of good resistants. This applies to hot or cold solutions, aerated, unaerated, or in the form of spray.

As mentioned in the section on acids, the protective oxide film on the chromium alloys is particularly susceptible to penetration by the chloride ion. This is especially true of chloride acid solutions, but to some extent also in neutral solutions. It is for this reason that solutions of the chlorides of copper, mercury, iron, tin, zinc, and aluminum are corrosive—at times extremely corrosive—to the chromium alloys even when alloyed and heat-treated to give maximum resistance. Such solutions are characteristically acid. A good example of corrosion rates is given in Table 182.⁸⁸

TABLE 182.—20 Cr 7 Ni vs. Chloride Solutions.

			Mg. per sq. dm. per day	
			20 Cr 7 Ni	20 Cr 7 Ni 2.5 Mo
Copper chloride,	50%,	boiling.....	110,000	150,000
Ferric chloride,	50%,	122° F.....	24,000	32,000
Zinc chloride,	78° Bé.,	95° F.....	10	
Stannic chloride,	sol.,	68° F.....	550	
Stannous chloride,	sol.,	122° F.....	65	
Mercuric chloride	0.7%,	68° F.....	210	
Mercuric chloride	0.7%	boiling.....	880	

Other tests,⁴⁰ in 27.5° Bé stannic chloride, gave rates as shown in Table 183.

TABLE 183.—Cr Ni Fe vs. Stannic Chloride.

		Mg. per sq. dm. per day	
		18-8	14 Cr 80 Ni
68° F., 3 weeks, quiet		317*	105
40° F., 1 day, agitated		448	172

* Grain boundary attack.

These results make clear another fact—when the solution is oxidizing the action is very much more rapid. Stannous chloride and zinc chloride are not oxidizing. Yet even the rates given for these are high enough to indicate that the metal is not completely passive.

Neutral chloride solutions—e. g. sodium chloride—are often not corrosive to properly produced 18-8. Yet this is on the active-passive borderline, as shown by the fact that pitting is not an infrequent occurrence with 18-8 in salt brines.

In neutral chloride solutions, in fact, the behavior of 18-8 ranges from completely passive to a condition of passivity over most of the surface but with localized points of rather rapid attack. In calcium chloride or sodium chloride brines of high concentration the normal condition seems to be one of complete passivity. This seems true also of dilute solutions. Yet the sensitivity of the alloy to cell attack resulting from circumstances such as contact with an external substance like glass rods used to hold specimens in laboratory tests, barnacles in sea water, oxide scale, or structure change as from the heat of welding, is pronounced. There is always the question, in using 18-8 with chloride solutions, whether external circumstances which might lead to localized attack can be avoided. It is definite enough that metal adjacent to welds will be likely to suffer localized attack in brines, in the case of ordinary 18-8 that has not been properly heat treated following welding. Yet on the other hand, it is true that this damage from the heat of welding is minimized if not entirely obviated by the use of a stabilizer. The use of a stabilizer, however, cannot be expected to prevent localized attack resulting from association with barnacles or other substances. As a preventive of attack from this source a molybdenum content in the alloy is at least partially efficacious.

An idea of corrosion rates of alloys that have been given a damaging heat treatment is offered by Table 184.⁶⁵ The tests were run for 20 hours at 86° F., in thoroughly aerated, agitated solutions.

TABLE 184.—*Chromium Alloys vs. Chloride Solutions.*

	Mg. per sq. dm. per day	
	5% NaCl	20% CaCl ₂
15 Cr	50	50
15 Cr 13 Ni	10	7
15 Cr 20 Ni	9	5

It is readily seen that neutral chloride solutions constitute a border-line condition, where the passivity of 18-8 is favored when the alloy is produced to offer its best front, yet where, even with every precaution taken, cells may be set up that cause pitting. These remarks apply to brines, to sea water, and possibly in lesser degree to lower concentrations of chloride salts.

It is rather important to have some idea of the rate of pitting attack when this does take place. In tests in calcium chloride brines at room temperature and less, pits have developed to a depth of .002 to .004 inch in 100 days. In the case of welded specimens, in calcium chloride brine at room temperature, no pits developed in the sheet remote from the weld, but in the zone adjacent to the weld the depths ranged up to .15 in. in 100 hours.

The 14 Cr 80 Ni alloy shows interesting behavior in salt solutions. Its tendency to develop pits is perhaps somewhat greater than that of 18-8, yet the rate at which pitting action goes on has been found in cases to be on the order of $1/7$ that of 18-8. The pits are characteristically broad and shallow as distinct from the straight-sided, deep pits on 18-8. This has been observed a number of times in exposure to sea water and to brines. Another feature of the 14 Cr 80 Ni is that its corrosion resistance is not damaged by the heat of welding.

The salt spray test⁹¹ has been widely used as a gage of quality for the chromium alloys. 18-8 has been required by the United States Government to be free from pitting or staining in 100-hours exposure; the lower chromium alloys, with or without nickel, are allowed somewhat more leeway. An investigation of salt spray resistance has been made by Arness and Ostrofsky⁴ on 12-27% chromium-iron alloys. In exposure up to 500 hours action varied from the faintest surface staining, to incipient pitting, and rusting. The test is not sufficiently sensitive to discover effectively weakness in the protective film that leads to corrosion under less favorable and more usual conditions—such for instance as submersion in sea water. Furthermore the test gives no indication of susceptibility to cell action that may be occasioned by a special circumstance in service.

Salt solutions on the alkaline side of neutral, in the absence of chlorides, are well resisted by the chromium alloys. Passivity is the normal if not the invariable condition for the 18-8 alloys and also the alloys of lesser chromium with or without nickel.

Of the alkaline salts, the hypochlorites^{71, 88} are quite distinctive in behavior from the others. These carry free chlorine as well as chloride, the free chlorine acting particularly to penetrate the protective oxide. Concentrated solutions^{82, 88} of either sodium or calcium hypochlorites are rapidly and destructively reactive, very dilute solutions³⁸ are not likely to destroy passivity. The critical concentrations lie intermediate. Attack by these solutions is likely to be localized and reasonably long duration of exposure is necessary before the severity of attack can be determined.

WATERS

The normal behavior of 18-8 in distilled, tap, or other fresh waters is one of passivity. Thus in the usual forms of exposure—submersion, partial

immersion, wet and dry exposure—the alloy remains substantially free of rusting and pitting. The activity-passivity border-line is rather remote from these conditions, although improper heat treatment or specially strong cell conditions will bring about rusting and incipient pitting. However, rusting and pitting when it does occur is of a superficial nature only.

For deep and rapid pitting to occur a strongly conducting electrolyte is necessary; fresh water of course does not qualify on this count. A superficial degree of rusting and pitting has been produced on 18-8 beneath a rag kept moist with tap water and resting for four weeks on the specimen. This so-called wick test constitutes a particularly severe cell condition; yet the poor conductivity of fresh water prevents the action from being more than a superficial one.

Spray tests⁴⁰ using city tapwater, made on specimens furnace-cooled from 1832° F. of several different compositions, indicated a very superficial degree of attack on 20 Cr alloys carrying nickel from 7 to 80%, over a 52-day test period. A number of 24 and 28 Cr alloys remained clean.

In sea water the situation is somewhat different, due both to the penetrating capacity of the chloride and the high conductivity of the water. Properly produced 18-8 exposed to sea water either submerged, half immersed, or in spray, will normally remain passive. On the other hand, when improperly heat treated or, particularly, when a cell is set up by some external situation such as a barnacle growth, action may be rapid. Whereas corrosion rates of passive 18-8 range below 1 mg. per sq. dm. per day, a large sheet exposed in Chesapeake Bay has been penetrated through .018 in. thickness in 7 days. This rapid attack was associated with deposits of marine life, and therefore the exposure condition was a special one, but this case indicates the rapidity of attack of a cell that is independent of the original quality of the metal. This moreover is not an isolated case.

The Ranger, an aircraft carrier of the United States Navy, was equipped with large welded 18-8 gasoline tanks into which sea water was run as the gasoline was drawn out. The material was carefully selected, heat-treated for the most part in the approved manner, and representative samples were tested with satisfactory behavior in salt spray. In spite of these precautions the tanks developed leaks in less than six months of shakedown cruises. Examination revealed numerous pits of various sizes, some of which had penetrated the walls of the tanks. The pits were more numerous in the neighborhood of welds and in areas improperly heat-treated, but were also scattered in areas over the entire surface.

The solution-cells which caused this action may have originated in several ways. They might have been caused by slight beginnings of sea growth, by adherence of floating particles, by imperfections or impurities

in the metal surface, or by some sort of damage to the surface during construction.

Chromium alloys that had been given damaging heat treatment were corroded as follows in fully aerated, agitated seawater, in 20-hour tests:⁶⁵

15 Cr	40 mg. per sq. dm. per day
15 Cr 13 Ni	10 mg. per sq. dm. per day
15 Cr 20 Ni	12 mg. per sq. dm. per day

Presumably the alloys were activated by the sea water.

In a series of tests⁴⁰ a number of alloys of commercial and laboratory production was submerged in New York harbor for three months. Commercial alloys of the 18-8 type were exposed in three conditions—cold-rolled, air-cooled from 1652° F., and heated 10 hours at 1200° F. Specimens carried pickled, and pickled and ground surfaces in each condition. The normal appearance following test was abundant pitting over the surface, and pitting beneath the fiber supports. Most specimens were completely penetrated. Marine growth was present on the specimens. Other alloys—8 Cr 20 Ni, 8 Cr 37 Ni, 12-16 Cr, 16-20 Cr were likewise actively pitted. A 28 Cr alloy was pitted somewhat on a ground surface but unaffected on a pickled surface, whereas 20 Cr 1 Cu was only faintly pitted, with two specimens remaining free of pits.

Bars of 18-8, 16 Cr 11 Ni, 17 Cr 11 Ni, 20 Cr 3 Ni, 20 Cr, 16 Cr 10 Ni, 20 Cr 80 Ni were exposed at half-tide level¹⁸ for three years in Southampton (England) harbor. Weight losses were all less than 1 mg. per sq. dm. per day, but all the specimens were locally attacked. Shell fauna had built up on the specimens, as well as a mixture of mud and oil.

Friend¹⁹⁻²³ has exposed 13.5 Cr .36 C in sea water at a number of locations for 5 to 10 years. In every case pitting took place, at rates ranging up to .01 in. per year, whether the specimens were continuously submerged or exposed at half-tide level.

Molybdenum-bearing 18-8 shows a very marked improvement over regular 18-8 in behavior to sea water. In the New York harbor tests referred to such an alloy remained completely free of any determinable action in the case of four specimens out of six; a fifth specimen had a single small pit remote from the support, another was corroded under the fiber support only.

This result has been confirmed in 90-day tests⁴⁰ in North Carolina baywater (Bogue Inlet, Swansboro). Molybdenum-bearing 18-8, in the case of three specimens, was completely free from attack; the fourth specimen was attacked beneath the Bakelite support to a maximum depth of .014 in. Samples of ordinary 18-8, low carbon 18-8, and titanium-bearing 18-8 were penetrated to a depth of .031 in. and greater. 14 Cr 80 Ni specimens were pitted in association with barnacles and at the supports.

The testing of the chromium alloys in fatigue brings out clearly the very high order of their resistance to the action of waters, as compared with ordinary steels. The rotating cantilever type of fatigue test is a very sensitive one for discovering a damaged surface, the drop in fatigue limit being the measure of damage.

Exposure of unstressed 12.7 Cr Fe (0.11% carbon) to a carbonate, fresh water has only a very slow damaging effect. According to a number of tests,⁴⁸ the resultant fatigue limit from 280-days exposure was on the order of 44,000 lbs. per sq. in., as compared with an air fatigue limit of 50,000 lbs. per sq. in.

Specimens tested in fatigue with the water stream at the same time passing over them were damaged as follows,⁴⁷ the figures in the last two columns representing the apparent "corrosion fatigue" limit, after 10^7 to 10^8 cycles at 1450 r.p.m.:

Alloy	Tensile Strength Lbs. per sq. in.	Fatigue Limit—Lbs. per sq. in.		
		Air	Fresh Water	Salt Water
11.8 Cr Fe (.11C)	80,000	41,000	34,000	14,000
13.3 Cr Fe (.13C)	91,000	59,000	40,000	13,000*
13.7 Cr Fe (.09C)	85,000	50,000	35,000	18,000*
18-8 (.16C)	125,000	50,000	50,000	25,000
17 Cr 25 Ni	115,000	54,000	45,000	34,000
17 Cr 25 Ni 3 Si	109,000	57,000	51,000	32,000
11 Cr 35 Ni	112,000	57,000	41,000	22,000

With chromium alloys, as with ordinary steel, salt water is much more damaging in this sense than fresh. Although no tests have been made on specimens previously exposed, unstressed, to salt water, specimens tested in fatigue while being washed with a stream of salt water were damaged as given above.

FOOD PRODUCTS

The chromium alloys are characteristically passive in exposure to food products. Corrosion rates in acid substances like fruit juices and milk and in neutral substances are very low, in most cases ranging under 1 mg. per sq. dm. per day, in some instances slightly above this, but in any case of negligible degree. Stainlessness is the common behavior, rusting rather rare and then usually confined to the zone of welds, and pitting seldom experienced.

Eighteen-eight and 14 Cr 80 Ni are widely used for food handling and processing equipment. From the standpoint of resistance to corrosion and tarnishing, neither has an advantage over the other, with the exception that the latter will not rust at the welds. Pitting, as already stated, is an

* Approximate.

uncommon occurrence. It has appeared in vinegar-salt mixtures and in boiling sugar-salt solutions. Pits in 18-8 under these conditions are likely to be deep ones, whereas those in 14 Cr 80 Ni are characteristically shallow. The chromium steels without nickel are less satisfactory than 18-8 and 14 Cr 80 Ni because of mechanical and working characteristics, and since these have a definite rusting tendency.

The behavior of 18-8 and 14 Cr 80 Ni in boiling fruit juices is interesting. These products of course are acid, containing tartaric, malic, citric, etc. Mention has been made earlier of the fact that boiling solutions of these acids are likely to destroy passivity and be very corrosive. This is not, however, experienced with boiling fruit juices of equivalent acid content. The results of Mrak and Cruess⁶¹ give rates of 5 to 62 mg. per sq. dm. per day for 14-17 Cr in handling tomato, apple, lemon, and red grape juices. Rates for 18-8 under the same conditions would undoubtedly be less.

A number of papers have been published covering the behavior of the chromium alloys with food products.^{3, 24, 29, 35, 37, 61, 70, 94, 97}

The possible toxicity of metal absorbed by foodstuffs from the chromium alloys has been the subject of investigations.⁹⁶ The conclusion is reached that the quantities of metal absorbed are so minute that they have no hygienic importance.

ATMOSPHERES

The more resistant of the chromium alloys are the only metals short of the precious metals that remain substantially unchanged in appearance in atmospheric exposure.^{17, 21, 23, 40, 105} These better alloys retain a large proportion of their brightness in prolonged exposure, in average rural and average urban atmospheres, are slightly stained in moderately sulfurous industrial atmospheres, are slightly stained to heavily discolored in strongly sulfurous industrial atmospheres, and generally rather heavily discolored in marine atmospheres.

The better alloys of the group, in the sense used in the preceding paragraph, are the 18-8 and high chromium (18-30%) types and the 14 Cr 80 Ni alloy. In strongly sulfurous atmospheres the addition of molybdenum to 18-8 is very markedly beneficial.

The corrosiveness of atmospheres increases with sulfur content. Generally speaking, whereas the lower chromium types may remain bright indefinitely in low sulfur atmospheres, they become discolored and finely pitted in moderately sulfurous atmospheres. Likewise, whereas the higher chromium types remain clean in moderately sulfurous atmospheres they discolor and tend to pit in strongly sulfurous atmospheres. In marine atmospheres the same general relation holds, the higher chromium alloys resisting discoloration and fine pitting better than the low chromium.

The superficial appearance of the alloys after exposure depends in some degree on whether the surface is freely washed by rain or not. Discoloration is more likely to occur where the metal is protected from the wash of rain yet freely exposed to atmospheric moisture, fog and dust.

Wide use is made of 18-8 in outdoor architectural construction, where continuously bright appearance is desired. The sheet metal work on the Chrysler and Empire State buildings in New York City is a well-known example. These surfaces, particularly where not in vertical planes, acquire a deposit of soot and dust like all surfaces, metallic or non-metallic, in urban exposure. These smooth metal surfaces, however, allow the wash of rain-water to clean the deposit rather effectively though not entirely. After several years of exposure now, these surfaces are substantially bright though carrying a thin soot and dust layer. Close examination of 18-8 test specimens exposed in urban air has revealed a tendency for rusting to occur—a very faint rusting. If this has taken place on the buildings referred to above, however, the evidences of it are completely obscured by the soot and dust deposit. Wiping with a dry cloth reveals perfectly clean bright metal.

Superficial pitting of the chromium alloys develops at random when the composition is not equal to the atmosphere, and when a cell condition is set up by a circumstance external to the metal, such as at the crossing of screen wires. This has been observed on screens of 18-8 and to a less extent 14 Cr 80 Ni in exposure for a year more or less in high sulfur industrial and in marine atmospheres, with a suggestion of pitting in rural atmosphere.

The effect of surface condition and heat treatment is often mentioned in connection with the behavior of these alloys in air exposure. Study of this ⁴⁰ revealed that in three-months exposure, 18-8 specimens behaved much the same whether in the cold-rolled, high-temperature annealed (favorable), or low-temperature annealed (unfavorable) condition. Ground surfaces in heavy sulfurous atmospheres were somewhat poorer than pickled or buffed surfaces and buffed surfaces only slightly, if at all, better than pickled. In saline air the heat treatment and surface treatment were of even less consequence to resistance. The high-nickel, low-chromium content alloys were practically insensitive to surface and heat treatment, whereas the nickel-free alloys were less satisfactory with ground surfaces, and better when hardened than when annealed.

HIGH TEMPERATURE CONDITIONS

The most useful of metals for handling conditions at high temperatures 12, 25, 51, 66, 86 are the nickel-chromium, nickel-chromium-iron and chromium-iron groups. This suitability centers around the resistance set up by the oxide coating that develops on the alloys in exposure to oxidizing atmospheres

and substances. The better alloys are useful at temperatures as high as 2100° to 2200° F.

Ordinary steels and iron begin to suffer progressive oxidation and scaling in the 1000° to 1200° F. range. Small additions of chromium or nickel or both are effective in raising this range somewhat. Alloys of the 14 Cr and the 18-8 types push the range up to about 1500° F. Lessening of the iron content with greater additions of nickel and chromium supply alloys that handle progressively higher temperatures. For the highest heat, 2000° to 2200° F., 15 Cr 60 Ni 25 Fe and particularly 20 Cr 80 Ni are the most suitable.

The presence of sulfur in hot oxidizing gases is likely to be damaging to the higher nickel-content alloys, and the lower nickel alloys are generally used. Reducing gases carrying sulfur are very much more damaging, since the sulfide coating that forms is less protective than an oxide coating. Such gases and substances therefore cannot be handled in the same high temperature range as oxidizing substances, a fact particularly marked with the nickel alloys.

Another type of substance more damaging than oxidizing atmospheres is alkali salt fusions, these tending to flux off the protective oxide coating on the chromium alloys. High nickel content is beneficial under such conditions.

Compositions of the commercial alloys used under heat may be grouped as follows:

- 15-20 Cr 50-80 Ni—Most resistant of the alloys in sulfur-free oxidizing atmospheres; wide use as electrical resistance elements.
- 15-20 Cr 25-50 Ni—Good oxidation resistance in gases with and without low contents of sulfur; reasonably cheap; good load carrying capacity.
- 20-30 Cr 12-25 Ni—Good resistance to higher sulfur content gases; good load carrying capacity.
- 18-8; 14 Cr—General purpose alloys for use below about 1500° F.
- 20-30 Cr—Best for extreme sulfur conditions; relatively low load-carrying capacity.

A large number of compositions, both within and without these ranges, is produced. Addition elements like silicon, tungsten, aluminum, are often present.

Failures of metal in heat applications occur by oxidation and scaling, intergranular disintegration, and—in the case of most failures—by over-stressing and cracking due to loading and thermal changes.

Oxidizing gas without sulfur.

An idea of the rates of oxidation of several alloys in the high temperature range may be gained from the various sets of data given below. Dickenson¹⁵ tested 14.7 Cr .26 C and 11.7 Cr 65 Ni in intermittent exposure over a wide temperature range. His cycle was 5½ hours at heat followed

by cooling and cleaning the specimen of scale. The scaling rates given in Table 185, developed over 18 cycles of heating, were found to be substantially constant with time.

TABLE 185.—*Metals vs. Oxidizing Atmosphere.*

Mean Temp. ° F.	Metal Oxidized—Mg. per sq. dm. per day		
	.30 C Steel	14.7 Cr .26 C	11.7 Cr 65 Ni
1067	990	<36	<36
1247	2,900	180	<36
1337	6,600	365	
1427	13,000	730	
1607	36,000	2,500	620
1607	34,000	2,900	400
1733	58,000	6,200	510
1877	130,000	51,000 (?)	730
2012	200,000	100,000	2,900

These data are particularly interesting in that they outline the temperature range over which one of the less heat resistant of the chromium alloy group is suitable, and the degree of improvement, in the high temperature range, offered by one of the better alloys of the group. It is common now to have 15 to 16% chromium rather than 12% in this latter type of alloy. The intermittency of exposure in this case made the test a more severe one, and yet one that corresponds to conditions often met in service.

Investigations of the 15 Cr 60 Ni and 20 Cr 80 Ni alloys in the form of wire resistance elements have been made.^{8, 34, 85} Under conditions so controlled that the wires remained at constant temperature even though the electrical resistance increased with time, the "life-to-failure" data on the alloys were as shown in Table 186.³⁴

TABLE 186.—*Chromium Alloys vs. Oxidizing Atmosphere.*

Temp. ° F.	Hours to Failure		Metal Oxidized—In. per yr.	
	20 Cr 80 Ni	15 Cr 60 Ni 25 Fe	20 Cr 80 Ni	15 Cr 60 Ni 25 Fe
1652*	636	529	.06	.08
1922	130	52	.53	1.4
2102	32	18	2.2	3.9
2282	12	5	5.9	14

* Wires at this temperature were 0.25 mm., at other temperatures 0.4 mm. in diameter.

Rohn's tests⁷³ are particularly interesting in that they cover a wide range of alloy compositions. The weight changes are average for successive one hour exposures, at 1832° F. and represent approximately constant rates of attack under intermittent heating and cooling. See Table 187.

Repetitions of heating and cooling are a more damaging condition than continuous heat. This fact is brought out in the results quoted below⁸⁵ on several specimens of 20 Cr 80 Ni from different producers, at 2092° F. In continuous exposure wires of .015 inch diameter had a life of 440 to 683 hours (approximately .15 to .10 inch per year oxidation rate), whereas in

TABLE 187.—Chromium Alloys vs. Oxidizing Atmospheres.

Ni	Cr	Fe	Mo	Scale Formed (Metal Plus Oxygen)*
				Mg. per sq. dm. per day
35	15	50		6000
22	16	62		4800
100				4800
63	15	22		720-3100
70	20	10		480
65	25	10		360
85	15			240
63	15	15	7	140
80	20			48-96
50	33	17		48

* Metal constitutes about three-quarters of the weight of oxide scale.

intermittent exposure to the heat the life was 53 to 80 hours (approximately 1.2 to .8 inch per year). Intermittency was in this case a more damaging condition by 8 to 9 times. The same effect on 20 Cr 80 Ni has been confirmed elsewhere.^{8, 34}

The damaging effect of intermittency on less resistant alloys at lower temperatures is suggested likewise by a comparison of data on 14.7 Cr .26 C .59 Si¹⁵ in intermittent exposure and on 13.12 Cr .32 C 1.32 Si³² in continuous exposure. The beneficial effect of the slightly higher chromium in the first alloy would tend to be offset by the higher silicon content of the latter. See Table 188.

TABLE 188.—Cr Fe vs. Oxidizing Atmospheres.

Temp. ° F.	Metal Oxidized—Mg. per sq. dm. per day	
	14.7 Cr .26 C .59 Si Intermittent Heating	*13.12 Cr .32 C 1.32 Si Continuous Heating
932		29
1067	<36	
1112		60
1247	180	
1292		120
1337	365	
1427	730	
1472		230
1607	2,500	
1607	2,900	
1652		320
1733	6,200	
1832		20,000
1877	51,000 (?)	
2012	100,000	50,000

* The assumption is made that the metal oxidized is three times the weight gain.

The more damaging effect of intermittency becomes most marked with this type of alloy at 1292° to 1472° F. Up to this range the oxide remains reasonably protective whether in intermittent or continuous exposure.

The rapidity with which the protective oxide forms on an alloy is important. An indication is afforded by the data in Table 189 on the 12-20 Cr 62-83 Ni range at 2012° F.⁹⁸

TABLE 189.—Cr Ni Fe vs. Oxidizing Atmosphere.

Exposure Period	Metal oxidized* Mg. per sq. dm. per day (approximate)
First hour	3,600-10,200
First four hours	1,110- 2,240
Three hours following the first hour.....	0- 390

* The assumption is made that the metal oxidized corresponds to three times the weight gain.

This comparison applies therefore to exposure conditions that are rather severe for the alloy tested, yet still on the safe and "protective-oxide" side. For less severe relative conditions, of course, the protective oxide is more rapidly formed and the oxidation both while it forms and subsequently very much less.

The effect of time on the rate of weight change has been determined³³ in tests over a 40-hour period in air. The weight change was determined at heat, so that the specimens were not in intermittent heat exposure. The results are given in Figure 50. The temperature was 2012° F., which is in the free scaling range for iron and 18-8, yet not for 27 Cr Fe.

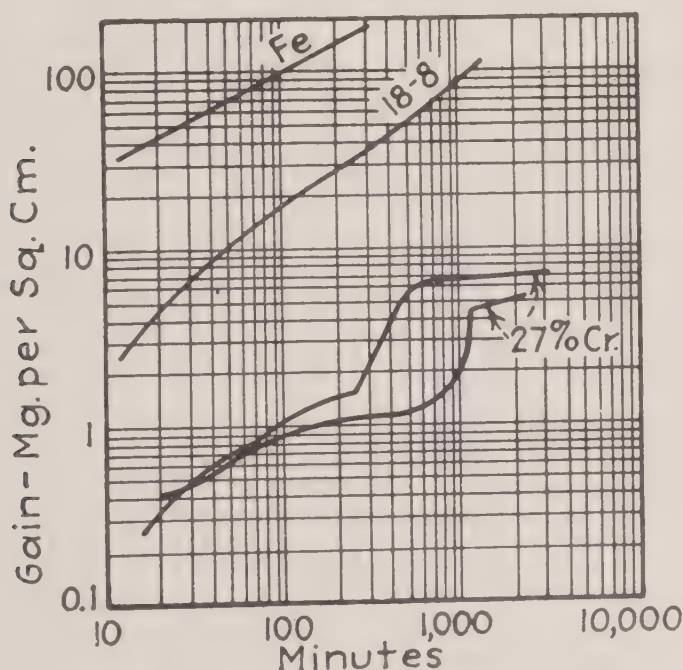


FIGURE 50. Chromium Alloys vs. Air at 2012° F.

In tests where specimens were exposed to pure oxygen continuously at temperature for 24 hours, ³² the oxidation rates in Table 190 were obtained on several alloys.

TABLE 190.—*Chromium Alloys vs. Oxygen Gas.*

	Metal Oxidized*—Mg. per sq. dm. per day			
	1292° F.	1472° F.	1652° F.	1832° F.
13.1 Cr	67	570	840	27,500
18.5 Cr	180	220	570	870
17.7 Cr 8 Ni	320	315	820	1,700
11 Cr 35 Ni	520	2,200	3,500	5,800
12 Cr 60 Ni	72	148	230	530

* The assumption is made that the metal oxidized corresponds to three times the weight gain.

These rates are lower than could be expected under repeated heating and cooling conditions. The effect of intermittency has already been brought out.

The gas content of the oxidizing atmosphere is somewhat of a variable, though, with the exception of sulfur dioxide in contact with the higher nickel alloys, not a really great one. Hatfield ³² compared the action of air, oxygen, carbon dioxide, and steam in 24 hour continuous-heat tests. The oxidation rate ranges in these four atmospheres for 18-8 and 12 Cr 60 Ni* are given in Table 191.

TABLE 191.—*Cr Ni Fe vs. Oxidizing Atmospheres.*

	Metal Oxidized*—Mg. per sq. dm. per day			
	1292° F.	1472° F.	1652° F.	1832° F.
17.7 Cr 8 Ni	66-300	120-330	140-1800	1700-6500
12 Cr 60 Ni	66-120	90-150	160- 420	330- 510

* The assumption is made that the metal oxidized corresponds to three times the weight gain.

No atmosphere of those used was outstandingly and consistently more, or less, damaging than the others.

In other tests ³⁴ at 1922° F. on 20 Cr 80 Ni and 18 Cr 65 Ni 15 Fe, in air and atmospheres of carbon dioxide, carbon monoxide, nitrogen, and oxygen the differences in damaging effect among the gases was much less marked than in those just given, for any single temperature.

Silicon is outstanding in improving oxidation resistance. The 8 Cr 3 Si alloy, used widely for automotive exhaust valves, is an example. This also has given extremely good results in laboratory tests.^{32,42} The beneficial effect of silicon when present in 18-8 and other chromium-nickel-iron and chromium-iron mixtures has also been pointed out.^{32, 42, 52, 53, 66}

Tungsten in 18-8 seems decidedly beneficial.³² Yet in the high nickel chromium alloys there seems no benefit⁸⁵ through tungsten additions. Molybdenum in these high nickel alloys has in cases been without benefit and in other cases mildly beneficial.^{34, 85}

*Not tested in air.

Oxidizing gas carrying sulfur.

Sulfur dioxide has essentially an oxidizing reaction on the chromium-nickel-iron alloys in the high temperature range, with the exception that the higher nickel alloys (over about 35%) are both sulfidized and oxidized in the range above approximately 1300° F. With the occurrence of sulfidization the usefulness of these alloys is lost.

Chromium is the essential element in building up resistance against sulfur dioxide, either pure or in air mixtures, in the 1000° to 2100° F. range. The best behavior is offered by alloys with about 30% chromium. With more chromium some resistance is lost. With chromium at 30%, nickel contents from 0 to 35% do not alter resistance, though of course nickel is desirable for the sake of mechanical strength. As already stated nickel above 35% lessens resistance.

The data in Table 192³² describe behavior of typical alloys in continuous exposure for 24 hours in sulfur dioxide, at different temperatures.

TABLE 192.—*Cr Ni Fe vs. Sulfur Dioxide Gas.*

	Weight Gain—Mg. per sq. dm. per day			
	1292° F.	1472° F.	1652° F.	1832° F.
Mild carbon steel	980	4160	17,700	
8 Cr 3 Si	52	120	450	320
13.1 Cr 1.3 Si	39	100	990	5800
18.5 Cr	45	54	82	140
17.7 Cr 8 Ni	140	160	180	260
17.7 Cr 7 Ni 4 W	20	39	53	82
10.9 Cr 35 Ni	29	41	41	790
11.7 Cr 60 Ni	33	500	5,500	9100

These tests did not take into account the damaging effect of intermittent heating and cooling. The good behavior of the tungsten 18-8 is notable. The order of oxidation rate for this would seem to be 60 mg. per sq. dm. per day of metal oxidized at 1292° F., to about 240 at 1832° F.

Reducing gases carrying sulfur.

These gases^{27, 40, 72, 81, 102} characteristically sulfidize the chromium-nickel-iron alloys. The action is a far more damaging one than oxidation,⁷² and the upper temperature limits at which the alloys are useful are much more confined. Seven-day tests at 625° F. in a mixture of hydrogen sulfide and natural gas led to corrosion rates on the order of 300 mg. per sq. dm. per day on 14 Cr, 15 Cr 60 Ni and 20 Cr 80 Ni.⁴⁰ Other tests at 900° to 950° F. led to penetration rates on the order of 120 to 160 mg. per sq. dm. per day for various stainless steels, and several times that for a 60% nickel alloy.

In Scholl's tests ⁸¹ in exposure at 900° F. for 28½ hours the data in Table 193 on sulfur combined with the alloys were obtained.

TABLE 193.—*Chromium Alloys vs. Hydrogen Sulfide.*

Metal	Weight Gain Mg. per sq. dm. per day
Mild steel	2900
8 Cr	2500
14 Cr	1650
19 Cr	530
25 Cr	530
18 Cr 75 Ni	5800
13.8 Cr 62 Ni	2900
14.7 Cr 35 Ni	2400
11.3 Cr 30 Ni	1600
17.3 Cr 25 Ni	530
26.1 Cr 21 Ni	530

A rate of 530 mg. weight increase, would correspond to somewhat over 530 mg. per sq. dm. per day of metal sulfidized. Even at 900° F. therefore only the better alloys of the group have reasonably good resistance.

Tests made ²⁷ in a zinc-roasting furnace have given interesting results with commercial heat-resisting alloys. The gases produced carried 5 to 6% sulfur dioxide, with condensed galena (lead sulfide) possibly present. The results are summarized in Table 194.

TABLE 194.—*Chromium Alloys vs. Hot Sulfur Gases.*

	Penetration Rate—In. per year	
	24 Hours at 1922° F.	96 Hours at 1652° F.
25-30 Cr	4.7-8.8	1.1-1.5
22 Cr 25 Ni	11	4.3
17 Cr 34 Ni	14	3.3
19 Cr 40 Ni	8.8	4.0
28 Cr 58 Ni	10.8	

Conditions within roasting furnaces are described by Brown.¹⁰ Rabble shoes operate in both reducing and oxidizing atmospheres high in sulfur.

Ammonia at high temperatures.

In respect to ammonia atmospheres, Vanick ⁹⁹ states that 16 Cr 15 Ni exposed for six months to a synthesizing ammonia atmosphere at 952° F., under 1500 lbs. per sq. in. pressure, was unusually resistant to the penetration of gases, and consequent deterioration. Chromium irons behaved well likewise. Ammonia under these conditions is reducing and actively attacks most ferrous and non-ferrous metals by virtue of the highly penetrative capacity of hydrogen.

The alloys have good resistance to nitriding conditions, involving the breakdown of ammonia.^{84,106} In European practice 25 Cr 20 Ni has been used

a great deal with success. According to Klouman⁴⁴ a minimum of 25% nickel seems necessary to prevent decomposition of the gas by the container rather than by the metal intended to be nitrided. Harsch and Muller³⁰ have reported that 12.5 Cr 62 Ni containers were very definitely more satisfactory than 13 Cr and 18-8.

Carburizing boxes.^{44, 93, 106}

Carburizing is done at 1450° to 1750° F. The 15 Cr 35 Ni and 15 Cr 60 Ni types are used very extensively for these boxes, with a normal life of 5000 hours and upward. The nickel largely prevents the absorption of carbon by the box. Deterioration on the inside is ordinarily no more rapid than oxidation on the outside. With high sulfur fuels it is customary to use 15 Cr 35 Ni, or alloys with lower nickel. Energizers of sodium salts are very damaging if allowed to escape to the outside walls.

Steam.

Cr Fe and Cr Ni Fe have been found to be much less susceptible to steam embrittlement in the upper reaches of steam temperatures than ordinary iron and steel. Fellows¹⁶ has indicated the much greater rate of hydrogen evolution from steel superheater tubes as compared with 16 Cr Fe operating in the same temperature range. According to Rummel⁷⁵ superheater tubes of 18-8 with temperatures on the fire side up to 1200° F. do not lead to serious breakdown of the steam.

Molten metals.^{31, 39, 44, 106}

The chromium-nickel-iron series are not as a rule useful in handling molten metals—tin, zinc, solder, babbitt, aluminum, brasses, etc. Lead is somewhat of an exception. Woodson¹⁰⁶ states that operating temperatures of 1300° to 1650° F. in the bath do not corrode the vessels rapidly if the lead is pure and cleaned daily, and that with proper care pots of 20 Cr 66 Ni will usually give 3000 to 6000 hrs. life at 1500° F. He also states that small additions of impurities, such as bismuth, antimony, etc., appear to accelerate corrosion. Corrosion is more rapid at the surface of the lead bath,⁴⁴ due probably to the slagging action of the lead oxide. The 15 Cr 35 Ni and 20 Cr 66 Ni alloys are much alike in behavior.¹⁰⁶

Fused compounds.

The heat-resistant alloys are used to a considerable extent in handling fused compounds in the heat treating of steel—, sodium, calcium, barium chlorides, cyanides, etc. With these corrosive action is more than appreciable, the nickel-bearing alloys behaving better than the straight chromium alloys. Caustic soda or potash at very high temperatures is rapidly corrosive. Thus salts that may alter to caustic, such for instance as sodium

carbonate or cyanide, will destroy a heat-treating pot in short order if the salts work out of the container onto the very hot outer surface.

Two-hour tests in various salts at 1472° to 1652° F.—calcium and sodium chloride, borax, sodium sulfate, sodium carbonate—have led to rates on the order of 1000 mg. per sq. dm. per day, and often greater. Rates as high as these would be entirely unacceptable in aqueous corrosion, yet with the heavy sections used in high temperature equipment and the much more rapid destruction of other materials, these rates often are within the acceptable range.

CHROMIUM ALLOYS

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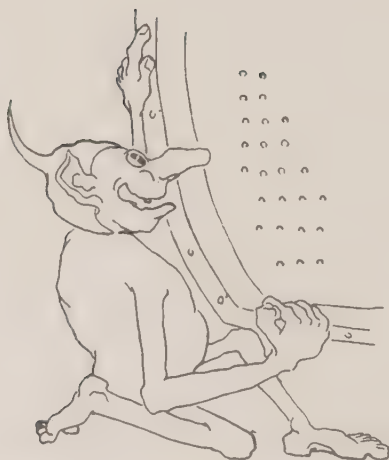
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Chapter XV

Chromium Plate

The effectiveness of chromium as an ornamental plating on steel and non-ferrous metals is plainly evident in the trim of motor-cars, in plumbing fixtures, and in innumerable other uses to be seen on every hand. Though not so well known to the layman, chromium plated tools, dies, etc., are already in rather common use, the layer of chromium supplying a smooth and hard surface that gives better results for many purposes than the unplated tool steel. There also is the field of use for chromium plate in which its value lies in resistance to corrosive conditions other than the atmosphere. The low coefficient of friction and the non-wetting property of chromium in contact with water and molten metals are further reasons for its use.

Metallic chromium up to now has been produced on a commercial scale only as an electroplate. The details of the different methods by which chromium can be plated and is being plated vary considerably, but the better practices in common use are similar in essentials; the chromium is plated from a chromic acid solution, containing a small amount of chromium sulfate, the energy being supplied by an electric current impressed between an insoluble anode and the object being plated as a cathode.

The conditions used in chromium plating* are far more uniform than those used with nickel plating. For practical purposes it may be assumed that the concentration of chromic acid is always between 200 and 400 grams per liter and the ratio of chromic acid to sulfate from 100 to 200. Occasionally solutions containing fluoride or fluosilicate, instead of sulfate, are used. The temperature is usually between 95 and 120° F., and the current density between 75 and 200 amperes per square foot (8 to 21 amperes per sq. dm.). Occasionally, especially for very thick deposits, temperatures up to 165° F. and current densities up to 1000 amperes per sq. ft. (110 amperes per sq. dm.) are used.

* W. Blum, private comment.

STRUCTURAL CONSIDERATIONS

Chromium is plated in a commercial way on all kinds of iron and steel—carbon and alloy steels, case-hardened steel, cast iron, etc.—on copper, brasses, bronzes, nickel, nickel-copper alloys, on aluminum, zinc, cadmium plate. With some metals as base the results are better, for various reasons, than with others. Chromium plate intended primarily as an abrasion resistant requires a hard base, such as case-hardened steel; the chromium is plated directly on the steel. Where good appearance in indoor atmospheric exposure is the sole requirement, the base may be any metal. For outdoor exposure the base is usually copper or its alloys or steel. In plating steel for outdoor exposure, e. g. automobile radiator shells, underlying coats of nickel and copper or nickel alone are essential, these serving a double purpose:—(1.) for the best results chromium must be plated on as highly buffed a surface as consistent with cost, this being more effectively obtained by buffing nickel and copper than steel; (2.) underlying coats give a much more corrosion resistant product. Likewise preliminary layers of nickel are frequently applied, before chromium plating, to brass, copper, and aluminum as base metals.

The thickness of chromium deposits varies from mere flash coatings up to over .001 inch. Deposits around .001 inch are usually not considered satisfactory because of relatively poor adherence and a tendency to crack. In present-day practice thicknesses of .00005 to .0001 inch are common for outdoor exposure; flash platings of .00001 inch and less are short-lived as protectives in outdoor exposure, though relatively satisfactory indoors. Underlying coats of nickel, or nickel and copper, on steel range up to about .001 inch in thickness, with the better results obtained with the thicker deposits. Preliminary nickel layers on brass and copper are usually .001 to .0003 inch; a greater thickness is applied to zinc base die castings.

In common with electroplated deposits of other metals, chromium layers characteristically are porous and often carry a fine network of cracks. Although these are apparent defects from the standpoint of corrosion resistance, it must be kept in mind that the advantages of chromium plate have achieved recognition in spite of the existence of porosity and cracks.

The continuity and effectiveness of chromium deposits are tested by various methods. The salt-spray test is commonly used for plated steel articles; the time that it takes for rust to appear and the characteristics of appearance are observed. This method gives a very rough idea only of the life that may be expected of the article. A period of 80 hours before rusting in the salt spray has been more or less arbitrarily chosen in one case as a desideratum for automobile parts, and plate has been produced

that will stand periods of 120 hours and even greater without signs of rusting. The conditions of exposure in the salt-spray test are severe, much more so than in ordinary atmospheres; its usefulness lies principally in comparing one specimen with another rather than in predicting behavior in atmospheric exposure.

The copper deposit test indicates areas on a chromium plated article where underlying steel or nickel is exposed, since copper does not plate out on chromium from a copper sulfate solution. In the hydrogen sulfide test the nickel exposed at discontinuities in the chrome layer becomes black and plainly visible, and in the ferricyanide test areas where underlying steel is exposed are indicated by the solution turning blue.

Baker and Pinner¹ investigated the protective value of chromium-plated steel, both with and without underlying layers of nickel and copper, using the salt-spray, copper and ferricyanide tests. The evidence from these tests that combination coats give better results than a coating of chromium alone is indisputable. In fact the authors drew the conclusion that "the protective value of a composite coating depends largely on the protection afforded by the underlying coats." In interpreting this conclusion it is necessary to keep in mind that the criterion of protective value referred to is the number of hours in the salt spray required for the specimen to become noticeably rusted. This criterion is but one of those involved in the practical use of chromium plate, another being the durability of the coatings themselves; from the latter standpoint chromium inherently is better than either copper or nickel.

Baker and Pinner found also that the nature of the combination layers, and the thickness of the layers individually, influenced the protectiveness. This is summarized in the following diagram. (Fig. 51).

By means of the copper-deposition test, it was found that in the case of chromium-plated steel with an underlying nickel layer, chromium deposits up to .000013 inch showed numerous fine round pores that decreased progressively in number with increase in thickness. Deposits above about .000017 inch in thickness carried fine cracks that became more pronounced with increase in thickness. The best protection offered by the chromium in the salt-spray tests was in the range of thickness where both the pores and cracks were at a minimum.

In studying the porosity of chromium plating on nickel, in thicknesses of chromium up to .00015 inch, Baker and Rente² established the existence of a point of minimum porosity for all bath compositions and temperatures investigated. Porosity as indicated by the copper deposition method varied in its nature and distribution with thickness of chromium: "With a thin deposit of chromium, the copper deposit is in the form of spots that are tiny, and evenly distributed over the surface. As the thickness of

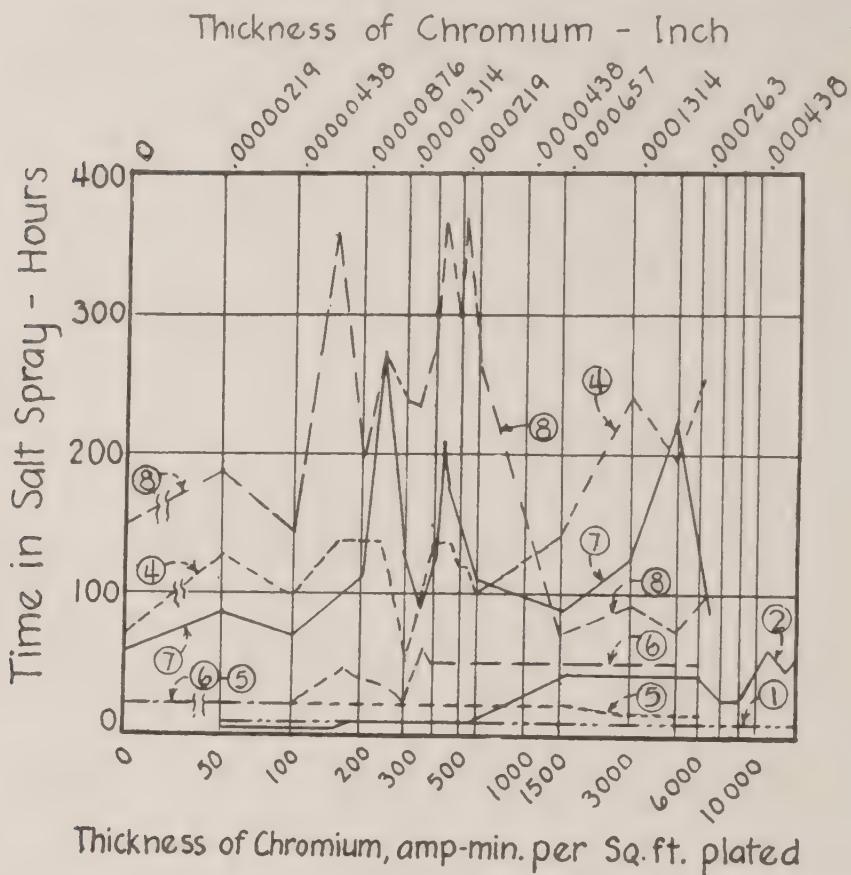


FIGURE 51. Chromium Plate vs. Salt Spray. Thickness of plate as follows:

- 1 Chromium—0.000002 to 0.00066".
- 2 Chromium—0.000002 to 0.00066".
- 3 Chromium—0.000013", on nickel—0.00004 to 0.00088".
- 4 Chromium—0 to 0.00026", over nickel—0.00026".
- 5 Chromium—0 to 0.00026", over "cyanide" copper—0.00029".
- 6 Chromium—0 to 0.00026", over copper—0.00026", over nickel—0.00018".
- 7 Chromium—0 to 0.00026", over nickel—0.00026", over copper—0.000094", over nickel—0.000088".
- 8 Chromium—0 to 0.00026", over nickel—0.00035", over copper—0.00028", over nickel—0.00018".

chromium is increased, the spots seem to group themselves in twos and threes. As the thickness of chromium is further increased the spots begin to arrange themselves in short wavy lines consisting of four or five spots in a line. These lines grow to a considerable length, containing 12 to 20 spots. They then break in pieces, and lines are formed at angles to these shorter lines.

"The crooked lines so formed tend to gather in bunches or tangles with more or less free space between the bunches. These bunches, up to the limit of the experiments, seem to get much denser and farther apart with increasing thickness of chromium."

Davies and Wright⁶ tested chromium-plated brass, phosphor bronze, copper and steel in the spray of sodium chloride (2.4%) and sulfuric acid (.05 normal) respectively, the thickness of the chromium being .0001, .0005, .001, and .002 inch. In 336 hours total exposure, during 103 hours of which the spray was applied, the non-ferrous base specimens were in good condition, with no variation in behavior with thickness of the plate. The chromium on the steel specimens afforded but poor protection, regardless of thickness, the initial pin-points of corrosion tending to grow laterally rather than in depth.

Blum, Barrows, and Brenner⁴ found that, when plated at higher temperatures (131° and 149° F.), chromium deposits reached a certain degree of porosity which did not increase with an increase in thickness.

PASSIVITY *

The corrosion resistance of chromium is due to its capacity to become and remain passive, a characteristic that chromium has in much greater degree than other metals. For the development and maintenance of this passive condition exposure in oxidizing substances is necessary; in fact the commonly accepted explanation of the passivity of chromium is the existence of a protective layer of chromium oxide. Among the exposure conditions in which chromium is passive are most if not all neutral reacting solutions (atmosphere, water, salt solutions) and many acid-oxidizing solutions. Chromium is or becomes active in acid solutions of relatively high acid strength and low oxidizing capacity. Without the protection of the oxide, the disintegration of chromium is rapid. In hydrochloric or sulfuric acid for instance the attack is rapid.

The corrosion resistance of chromium, dependent on the presence of the oxide, is destroyed when the oxide is dissolved or damaged.

TWO-METAL GALVANIC CORROSION

In its galvanic relationships, chromium in the passive state acts as a very cathodic (noble) metal. It is only in exposure conditions where chromium is in the passive state that it finds commercial use. In galvanic couples of passive chromium and iron, the iron tends to suffer accelerated corrosion in the presence of aqueous solutions, e. g. water and moist atmosphere. The chromium tends to remain unattacked. Chromium-plated steel carrying pin-holes and without an intermediate layer of other metal, characteristically bleeds rust through the pin-holes, in exposure to the weather. The size of the holes in the chromium does not seem to increase nor is there a tendency for the chromium to become loosened, even over a long

* See chapter on Chromium Alloys for discussion of passivity.

period of exposure. The importance of decreasing the porosity of chromium plate on steel is obvious, and it is due in part to this galvanic relationship and to the fact that porosity in chromium layers is never entirely eliminated that in usual procedure intermediate layers of copper and nickel are applied. Although in galvanic couple with either nickel or copper, chromium is cathodic as it is with steel, the tendency for either nickel or copper to suffer accelerated action is largely negligible and for the most part probably non-existent in exposure to the atmosphere and to water. In exposure to acid solutions the tendency for nickel or copper to suffer is pronounced, and until porosity of chromium plate is entirely eliminated its usefulness in handling acid solutions must necessarily remain limited.

In couples of chromium with aluminum, zinc, and cadmium, chromium likewise is cathodic. Whether the other metals will suffer accelerated attack in normal atmospheric exposure is problematical; certainly the film-forming characteristics of these metals would tend to repress such acceleration and might prevent it in most cases.

AQUEOUS CONDITIONS

In outlining the behavior of a chromium-plated article to aqueous conditions it is convenient to make a distinction between the behavior of the chromium itself, the behavior of the base metal, and the behavior of possible intermediate layers of nickel or copper. It is necessary further to keep in mind that the thickness of the layer of chromium is almost always well under .001 inch and commonly is on the order of .00002 to .0001 inch, and that of intermediate layers of nickel and copper seldom more than .001 inch. The limits for chromium are set by such factors as adherence and cracking tendency rather than by cost considerations. Chromium plate, therefore, can have practical virtue as a corrosion-resistant material only under conditions where the corrosion rate of either the chromium deposit or the intermediate layers is very low. Where these corrosion rates are low the protective value then depends on how nearly free from porosity the plate may be. Although conditions in which a metal has almost absolute resistance to corrosion are relatively few, it seems to be true that the resistance of chromium to the atmosphere approaches the absolute. This of course is its *raison d'être* as a decorative. Piersol¹⁷ has stated that it is reasonable to expect a life of 5 years for chromium-plated automobile trimmings and ten years for plumbing fixtures. These limits are determined, not by corrosion of the plate, but rather by mechanical failure of the plate, and corrosion of the metal on which the chromium has been plated. Automobile trimming is exposed only intermittently to the weather and usually is wiped from time to time. Plumbing fixtures are exposed indoors.

The most important contribution to knowledge, to date, of outdoor behavior of chromium plate is the exposure tests in which the American Electroplaters' Society, The American Society for Testing Materials, and the National Bureau of Standards have cooperated. Blum, Strausser and Brenner ⁵ have given a description of these with the results at the end of 18 months. Three types of exposure were used: (1.) marine, at Key West, Fla., and Sandy Hook, N. J., (2.) industrial, at New York City and Pittsburgh, (3.) suburban or rural, at Washington, D. C., and State College, Pa. The authors concluded as follows:

(1.) A very thin deposit of chromium, such as .00001 in., usually reduces the protective value of composite nickel and copper plate and particularly pure nickel plate. Chromium coatings about .00002 to .00003 in. add very little to the protective value, but maintain their bright appearance owing to the resistance of the chromium to tarnish. Relatively thick chromium coatings, .00005 to .0001 in., improve the protection against corrosion particularly in an industrial atmosphere.

Specimens plated to a total thickness of .001 in., one series with a nickel underlayer and chromium surface, and the other series with copper and nickel underlayers and chromium surface gave results as listed in Table 195 in 18-months exposure.

TABLE 195.—*Chromium Plate vs. Atmosphere.*

	Ni-.001" Cr-.00002"	Cu-.0005" Ni-.0005" Cr-.00002"
State College	98	97
Washington	94	95
Key West	58	40
Sandy Hook	51	46
New York	72	68
Pittsburgh	23	20

The heavy corrosion at Pittsburgh as compared with New York, and the moderately heavy corrosion at the sea coast as compared with that at the rural locations are to be remarked. The higher the score the better the behavior, in accordance with the following relation.

Per Cent Score	Per Cent of Surface Rusted
100	0
80	0-5
60	5-10
40	10-20
20	20-50
0	50-100

In other types of exposure information on the behavior of chromium is meager. In salt solutions and water its resistance seems to be remarkably high. In strongly oxidizing acid solutions it is definitely good, but against

acids that are not strongly oxidizing—comprising most acid solutions—chromium does not stand up. In considering the durability of a chromium-plated object as a whole against acids we are confronted with the fact that nickel and copper, and any of the metals that may be used as the base metal or as intermediate layers, are acted upon in a degree that must be considered fairly rapid in view of the thinness of these intermediate deposits. There is too the further consideration, already mentioned, that base metal or intermediate layers exposed at discontinuities in the chromium may suffer accelerated galvanic attack.

Several quantitative tests have been made on the behavior of solid chromium in acid solutions. From these it can be concluded that hydrochloric, sulfuric, and acetic acids are characteristically strongly corrosive and that nitric even in fairly high concentrations may be corrosive. In Table 196¹⁰ chromium was immersed in quiet acid at 59° F. for 24 hours. The chromium was not electrolytic but cast.

TABLE 196.—*Chromium vs. Acids.*

	Mg. per sq. dm. per day
Hydrochloric, conc.	20,000
Nitric, 32%	60
Sulfuric, 17%	140

In the tests²¹ in Table 197, 99.8% pure solid chromium, likewise not electrolytic, was immersed 24 hours in cold acid and 1 hour in hot.

TABLE 197.—*Chromium vs. 10% Acid Solutions.*

	Mg. per sq. dm. per day	
	Cold	Hot
Nitric	13	<24
Sulfuric	10	1,000,000
Hydrochloric	77,000	3,000,000
Acetic	130	720
Phosphoric	<1	<24

Schwartz²² exposed chromium-plated steel specimens to air saturated with gases held in closed containers, for 192 hours, with the weight losses shown in Table 198.

TABLE 198.—*Chromium Plate (Steel) vs. Moist Gases.*

	Mg. per sq. dm. per day
Ammonia vapor	<27
Hydrochloric fumes	350,000
Nitric fumes	3,200
Hydrogen sulfide fumes	+

Of course it was the steel base that yielded these rates. It is likely that nitric fumes have no specific action on chromium itself, yet chromium plate

cannot be expected to protect any base if the metal used for the base has not, in itself, reasonably good resistance to the corrodent.

In qualitative tests, Schwartz further observed that chromium-plated iron exposed for weeks to the corrosive atmosphere of a laboratory was apparently unaffected, and that when immersed in tap water for three weeks there was no evidence of corrosion or loss in luster. A specimen immersed in boiling concentrated nitric acid for two hours remained apparently unaffected. The thickness of the layer was not stated.

Enos⁸ has compared the behavior of steel with chromium-plated steel in exposure to the outdoor atmosphere and to distilled water respectively. The weight losses of the plated specimens were high if the action that took place was concentrated on the iron exposed at pores or cracks. The conclusion is inevitable that these specimens had unsatisfactory behavior. See Table 199.

TABLE 199.—*Chromium Plate vs. Atmosphere, Water.*

	Mg. per sq. dm. per day	
	Outdoor 47 days	Distilled Water 21 days
Steel	?	25
Chromium-plated steel3	5.8

Murakami¹⁵ has tested chromium-plated steel, copper, and brass specimens under various conditions. Briefly, his results indicate good resistance of chromium plate to the atmosphere and poor resistance to some strong acids. Chromium-plated specimens exposed in various atmospheres gave the results in Table 200. The current used in plating was 15 to 20 amperes per sq. dm.

TABLE 200.—*Chromium-Plate Exposure.*

Atmosphere	Base	Plating time	Testing time, days	Change
Hydrogen sulfide	Iron	10 min.	7	Rust
Outdoors	Iron	10 min.	24	Rust
Laboratory	Iron	10 min.	24	Rust
Laboratory	Iron	20–30 min.	26	No change
Outdoors	Iron	20–30 min.	25	No change
Laboratory	Iron	over 30 min.	over 180	No change
Outdoors	Copper	10 min.	43	No change
Hydrogen sulfide	Copper	10 min.	43	No change
Laboratory	Copper	10 min.	43	No change
Laboratory	Copper	30 min.	over 180	No change
Outdoors	Brass	10 min.	43	No change
Laboratory	Brass	30 min.	over 180	No change

The great difference in behavior between specimens of chromium plate of different producers is a point that must always be kept in mind when interpreting behavior, both qualitative and quantitative. Some expression

of this variable is afforded in the results of tests on the effect of rubbing chromium plate with cleaners.¹³ Yellow brass pipe carrying .00015 in. plate of nickel and .000009 in. plate of chromium began to show brass after 1 hour 15 min. of rubbing. A red brass fitting, product of another plater carrying .000055 in. chromium, after 6 hours rubbing was only very lightly scratched, brass showing in a few very small spots. The difference was due of course not to a difference in quality of the plate. The example illustrates, however, the order of difference that may be expected if the part is not ordered to a definite specification as to thickness of the plate.

Similar specimens were further tested by suspending in a urinal for 43 days. On subsequent scouring with a moderately abrasive scouring powder a few small groups of tiny spots where chromium had been removed appeared on the yellow brass specimen, and a very large number of spots on the red brass specimen.

Chromium-plated automobile parts, marine hardware and plumbing fixtures have now been in use for years. Although the behavior in cases have been unsatisfactory, the important point is that in a great many cases the results have been perfectly satisfactory.

In sea water submersion tests, according to Sutton,²³ chromium deposits .0015 to .0025 inch thick direct on steel led to severe pitting of the steel at points over the surface.

McAdam¹⁴ compared the behavior in corrosion fatigue of an alloy spring steel and the same material plated directly with chromium, the exposure condition being a stream of fresh water. No definitely better behavior was observed for the plated specimen. In view of the probable discontinuities in the plate and the tendency for the concentrated stress set up by bending to rupture the coating, this is not surprising. Honegger (see Reference⁹) likewise found little if any benefit of chromium plate on steel in steam or water, under fatigue stresses.

ELEVATED TEMPERATURES

Chromium as an alloying element in iron and nickel has notably good high-temperature properties; by this is meant that the rate of penetrating deterioration of these alloys, thanks to the chromium, in exposure to gases at high temperatures is extremely low. This subject is covered in another chapter.

In oxidizing gases chromium, according to Humphries,¹² does not tarnish or heat tint in the range below about 650° F.

A useful survey of the behavior of chromium in hot gases has been made by Hatfield.¹¹ He exposed specimens of cast 98.1% chromium to a number of conditions, with the results shown in Table 201.

TABLE 201.—*Chromium vs. Hot Gases.*

	1292° F.	Gain in weight Mg. per sq. dm. in 24 hrs.		
		1472° F.	1652° F.	1832° F.
Oxygen	47	97	220	630
Steam	5	37	117	210
Carbon dioxide	27	34	130	308
Sulfur dioxide	16	39	320	360

Assuming the oxidation product to be chromic oxide, a gain of 10 mg. per sq. dm. would correspond to an oxidation rate for chromium of about 20 mg. per sq. dm. per day (.004 in. per year). The possibility that the rate over longer periods would have been somewhat less should of course be kept in mind. In any case the extreme thinness of chromium plate would not suggest its permanence as a protective in the higher temperature range above 1200° to 1300° F.

One use made of chromium-plated iron at elevated temperature has been airplane exhaust manifolds. The plate has been a reasonably satisfactory protective against rusting up into the 800° to 1000° F. range.

In considering chromium plate in high temperature exposure it is well to distinguish between the different factors involved. In the first place the rate of deterioration of the chromium, in view of the thinness of the deposit, must be extremely low. Then too the rate of deterioration of the metal exposed at cracks and pores in the chromium layer must be reasonably low. Also, the adherence of the plate to the underlying metal must persist in the elevated temperature range and through wide changes in temperature, in spite of conflicting expansion coefficients. Experience has shown that the properties of chromium plate in these respects are favorable for some purposes. In other cases unsatisfactory results only have been obtained.

Tests on chromium plate for five months at temperatures up to 1380° F., for a year at 840° F., and for 1000 hours at about 1110° F. have been reported as encouraging.*

In the glass industry chromium, plated directly on cast iron pressure molds, has been found to prolong considerably the life of the molds. This use involves temperatures of 1470° F. and higher, probably not exceeding 1730° F. ordinarily. The lack of adhesion between the chromium and the glass is important. At these temperatures the chromium plate tends to diffuse in the cast iron, though at a slow rate. Temperatures up to 2370° F. are sometimes involved, and then diffusion of the chromium into the base metal is relatively rapid, the chromium disappearing entirely in places after a few days.

* F. M. Becket, private communication.

Chromium-plated brass dies are useful in casting lead storage battery plates, the molten lead having no effect on the chromium. In fact chromium plate has good resistance to the metals melting at low temperature.

Humphries¹² records that chromium plate has been used as oven linings without raising, checking or discoloration of the coating, and that chromium-plated valve stems of internal combustion engines and chromium-plated steel pyrometer tubes are heated and cooled repeatedly without scaling. Phillips and Macaulay¹⁶ tested chromium plate about .0001 inch thick up to 450° F. and found that it did not peel. On the other hand Porter¹⁸ relates that attempts to obtain a chromium deposit on steel for use at 1400° to 1500° F. led to discouraging results, oxidation of the underlying iron leading to peeling and cracking. In only one case was a deposit obtained that stood up for more than 300 hours, the majority failing within 48 hours.

SULFUR SUBSTANCES

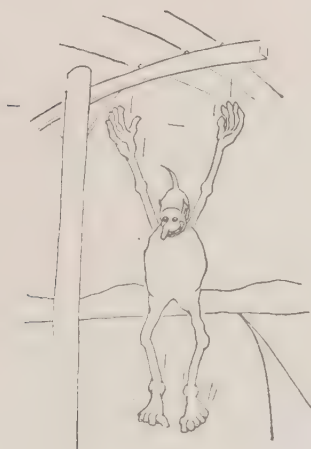
One of the more important fields in which the resistance of chromium is outstanding is that of reduced sulfur compounds, including hydrogen sulfide, sulfurous solutions, and sulfur-bearing organic compounds. In oil-refining such substances are the source of much difficulty with corrosion of ordinary equipment. Sixty oil tanks about ten feet in diameter and fifty feet high, were chromium plated, and after two years' use showed no signs of failure, whereas unprotected steel normally lost as much as $\frac{3}{4}$ inch thickness in a year.³ Chromium-plated still plugs, according to Egloff,⁷ have given good service where particular care in plating was taken. Others have found the results with chromium plating rather disappointing in oil-refining work.²⁴ For small parts such as thermo-couple wells plating is satisfactory, but less so for tubes and other large equipment.

CHROMIUM

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Chapter XVI

Nickel-Iron Alloys

GENERAL

The simple binary alloys of nickel and iron form a group of importance industrially because of special physical properties. The alloy with 36% nickel, known as Invar, has an invariable coefficient of expansion within the range of ordinary atmospheric temperature. The 50% and 80% nickel alloys have special magnetic characteristics to give them importance. Other alloys in the series are characterized by other physical properties that scarcely warrant outlining in the present discussion.

Even though the simple nickel-iron alloys have reasonably good corrosion resistance, this property practically never leads in itself to their use. It is fortunate that Invar does not rust freely in the atmosphere, since this means that Invar measuring tapes do not require the protection of paints or metal coatings to make them serviceable in normal service. The other alloys of the series are likewise far less prone than ordinary iron and steel to rust from moisture.

ACID SOLUTIONS

It is believed sufficient for the present purposes to give the results of a few tests on nickel-iron alloys. In this way a general idea of behavior may be gained without the necessity for detail that might be unjustified considering that the alloys are not used primarily because of corrosion resistance.

In resistance against acids these alloys are generally intermediate between nickel and iron, as would be expected. The data in Table 202² supply rates for three alloys together with nickel (98.3%) and electrolytic iron, in sulfuric acid at room temperature. The tests ran for 2 to 6 days under alternating immersion conditions. In concentrated acid the alloys were apparently better than nickel, as well as iron.

The action of various acids on iron alloys with 25% and with 38% nickel respectively is compared in the data in Table 203.⁸ The tests were made at room temperature over a 24-hour period, presumably in quiet submersion.

TABLE 202.—*Nickel-Iron vs. Sulfuric Acid.*

Acid Conc. %	Corrosion Rate—Mg. per sq. dm. per day				
	98.3% Nickel	78.5% Nickel	47.9% Nickel	37.6% Nickel	0% Nickel
5	250	350	1000	1630	3,300
10	300	680	1380	1710	4,020
25	290	1050	910	950	15,200
50	450	540	250	520	2,300
75	635	160	100	180	350
96	495	366	54	309	1,120

TABLE 203.—*Nickel-Iron vs. Acids.*

	Corrosion Rate Mg. per sq. dm. per day	
	25 Ni 75 Fe	38 Ni 62 Fe
Sulfuric acid 10%	165	60
20%	135	60
Nitric acid 32%	25,000	52,500
Hydrochloric acid 19%	330	285
Acetic acid, glacial	117	210

Another set of data, covering the action on 25 Ni 75 Fe of sulfuric, nitric and hydrochloric acids in quiet room temperature exposure of 24 days, is given in Table 204.⁵

TABLE 204.—*Nickel-Iron vs. Acids.*

	Corrosion Rate—Mg. per sq. dm. per day			
	59° F.	104° F.	140° F.	176° F.
Sulfuric acid				
12%	70	330	250	450
38%	120	450	1,060	1,640
63%	210	440	760	1,620
Hydrochloric acid				
2%	70	460	1,190	2,120
9%	160	1,760	4,180	20,920
17%	360	6,970	38,070	62,700
Nitric acid				
5%	10,560	17,440	20,900	25,950
32%	74,500	86,880	87,210	101,030

NEUTRAL SOLUTIONS

In neutral solutions—waters and salt solutions—the alloys behave much better than ordinary iron and steels, yet are less resistant than pure nickel. Submerged in quiet salt solutions at room temperature for 30 days a 30% nickel iron was attacked at the rates in Table 205.⁵

TABLE 205.—*Nickel-Iron vs. Salt Solutions.*

	Mg. per sq. dm. per day
Ammonium chloride 5%	14
Magnesium chloride 1%	3
Sodium sulfate 10%	4
Magnesium sulfate 5%	4

In tests in which specimens were alternately submerged and withdrawn from a 5% solution of sodium chloride, the rates in Table 206 were obtained.²

TABLE 206.—*Nickel and Iron Metals vs. Sodium Chloride.*

	Mg. per sq. dm. per day
Electrolytic iron	460
38 Ni 62 Fe	28
80 Ni 20 Fe	2.5
Nickel	5

In other tests ⁴ the comparison was obtained as shown in Table 207. The tap water and sea water tests ran 64 days, quiet, the other ran 52 days.

TABLE 207.—*Nickel-Iron vs. Water.*

	Corrosion rate—Mg. per sq. dm. per day	
	Ordinary steel	26 Ni 74 Fe
Tap water	8.2	4.1
Sea water	11	5
Wet and dry alternating	28	2.3

Friend ³ exposed a bar of 80 Ni 20 Fe for three years in Southampton (England) harbor. The corrosion rate was less than .1 mg. per sq. dm. per day, although there was widespread incipient pitting. Ordinary steel was corroded evenly at a rate of 8 mg. per sq. dm. per day. All specimens acquired a mass of fauna and mud that was believed to have suppressed corrosion.

ALKALINE SOLUTIONS

The resistance of iron and steel to strong caustic alkaline solutions at ordinary temperatures is very high, and nickel additions ordinarily give only appreciable improvement. In the more dilute solutions nickel additions would be beneficial in the same sense that nickel improves the resistance of iron to neutral solutions. Likewise, in strong hot caustic nickel is decidedly beneficial, and actually used commercially for improving the behavior of cast irons. The rates given in Table 208 were obtained on specimens submerged 54 days in a caustic evaporator in which the caustic soda, made by

TABLE 208.—*Nickel-Iron vs. Caustic Soda.*

Nickel Content of Cast Iron	Mg. per sq. dm. per day
0	366-458
3.5	235
5	247
15	152
20	17
30	2

the "ammonia-soda" process, was concentrated from 50 to 65%, under vacuum of 26 in.⁷

Other data on the behavior of nickel-iron alloys to hot caustic are given in the chapter on iron and steel.

ATMOSPHERE

Behavior in atmospheric exposure carries great significance for these alloys, even though this may never be the first consideration in their practical use. Nickel has the general effect of improving the resistance of iron to the atmosphere. Nickel fails, however, to bring about the degree of resistance that the chromium in stainless steels confers. The nickel iron alloys can scarcely be considered generally stainless or rustless.

There seems to have been made no detailed study of this question. In some tests,⁷ in which nickel-iron alloys were exposed two years in outdoor industrial atmosphere (Bayonne, N. J.) it was observed that the rust coating that developed on the 50% and 60% nickel alloys was only loosely attached to the metal, flaking off to reveal a bright metallic surface beneath. This is, of course, unlike the behavior of ordinary iron and steel, on which the rust is ordinarily very adherent.

In another set of tests⁷ specimens were exposed almost two years in industrial, rural and marine atmospheres respectively. The 20 Ni 80 Fe alloy was definitely inferior to the alloys with greater nickel, up to 60%. The surface on the former was deeply corroded beneath rust, whereas with the others the original surface had corroded away but the attack was not so deep. The original grind marks on the 60 Ni 40 Fe alloy were actually visible after marine exposure.

The improvement conferred by nickel is most marked in less severe exposure, as indoors, where rusting itself may be entirely prevented.

Sands⁹ has made the following statement:

"Polished Invar is highly resistant to atmospheric corrosion as well as to attack by fresh or salt water. Invar instruments may be left for long periods of time in moist atmospheres, under water, or even in steam without noticeable effect. But while the corrosion resistance is excellent, it is not perfect, and it is wise to keep Invar apparatus greased when not in use, especially in tropical climes. It is important to prevent inception of attack, for once started extensive damage may be done."

HIGH TEMPERATURES

Nickel-iron alloys are not considered heat resistant in the same sense that the chromium-nickel-iron alloys are. In fact a nickel addition to iron is not in itself sufficiently beneficial to be widely important, either in raising the temperature range in which iron may safely be used or in suppressing

rates at any given temperature. Dickenson¹ exposed specimens for successive periods totalling 100 hours, at each of several high temperatures. Between each period the specimens were scraped free of scale. The results are given in Table 209.

TABLE 209.—*Nickel-Iron vs. High Temperatures.*

Temp. ° F. Electric furnace	Loss by scaling—Mg. per sq. dm. per day	
	.30 C Steel	25 Ni 75 Fe
1067	996	180
1247	2,900	810
1335	6,600	1,800
1427	13,000	4,000
1607	36,000	20,000
Gas furnace		
1607	34,000	8,500
1731	58,000	36,000
1877	130,000	77,000
2012	200,000	160,000

Specimens of mild carbon steel and 36 Ni 64 Fe gained in weight as shown in Table 210 over a 24-hour period.⁶

TABLE 210.—*Nickel-Iron vs. High Temperatures.*

Gas and Temp.	Gain—Mg. per sq. dm. per day	
	Mild Carbon Steel	36 Ni 64 Fe
Oxygen		
1292° F.	1,040	412
1472° F.	2,970	972
1652° F.	8,340	1,400
1832° F.	17,860	2,550
Steam		
1292° F.	365	316
1472° F.	2,197	1,338
1652° F.	7,493	3,620
1832° F.	23,100	5,454
Carbon dioxide		
1292° F.	1,000	278
1472° F.	3,675	1,000
1652° F.	7,500	2,540
1832° F.	9,350	3,075
Sulfur dioxide		
1292° F.	985	2,000
1472° F.	4,160	14,000
1652° F.	17,700	20,000
1832° F.	converted	26,000

It is well to point out here that the nickel-iron alloys behave at high temperatures more nearly like ordinary iron and steel than like the "heat-resisting" alloy group.

NICKEL-IRON ALLOYS

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Chapter XVII

Nickel

Nickel is one of the more versatile metals, combining mechanical characteristics on the order of those of mild steel, relatively high degree of corrosion resistance, appearance of some aesthetic value, favorable working quality, and availability consistent with its diversified uses. The cost of nickel is high, reflecting mining, metallurgical, and mill factors.

Sheet, rod, and forging stock is ordinarily of 99% purity, with manganese and iron as the chief impurities. A grade containing up to 5% manganese is used in certain high-temperature applications. Nickel may or may not carry cobalt as an impurity, depending on the refining process; it has not been demonstrated that the effect of the presence of cobalt is either harmful or favorable.

Nickel has resistance of practical importance against most of the groups of corrodents. It is effectively resistant to acid, neutral, and alkaline conditions in general; it has certain definite advantages as a construction material for handling food products; in resistance to oxidation it is capable of operating at higher temperature than ordinary irons and steels and many of the common non-ferrous metals; its resistance to the milder forms of ordinary atmosphere gives it decorative value.

The natural reactivity of nickel, as indicated by its electrochemical behavior under a number of corrosive conditions, is higher than its general corrosion resistance would lead one to expect. There is a definite tendency of nickel to become passive but this is so undependable in its action as to be of doubtful practical significance. In certain cases, as in concentrated nitric acid at low temperatures, the effect is strong. In the exposure conditions which nickel can usefully handle, its effect is less obvious.

NICKEL PLATE

Nickel plating ^{1, 49, 50} is an effective commercial means for giving metal surfaces a bright and more or less permanent white appearance for use in atmospheric exposure. Steel, brass, and copper are the commonly employed base metals, and zinc and aluminum are occasionally used. Chromium

plate usually carries underlayers of nickel plate, an arrangement that makes possible a more nearly perfect chromium layer and improves the corrosion resistance of the article. The degree of protection afforded by nickel plate varies with a number of factors, particularly the thickness of the plate, and the type of atmosphere.

The two characteristics that chiefly limit the usefulness of nickel plate are the porosity and the thinness of the plated layer. It has so far been impossible to produce a perfectly non-porous film of metal, true of other metals as well as of nickel. Obviously enough, the base metal is exposed at these pores, which become loci for the accumulation of moisture-absorbing salts, with the result that galvanic cells often are set up. With steel as the base metal the corrosion may be relatively rapid. Pores and imperfections in the plate are due to several factors—surface defects in the base metal, foreign material adhering to the base metal, solids carried over in the plating bath, and the deposition of gas bubbles along with the nickel. Careful control of these factors and the use of thicker deposits of nickel tend towards lessened porosity; intermediate wiping is beneficial.

The thinness of deposits—usually .001 inch and less—means that even slight loss from corrosion or abrasion may be serious. Rain spots and tarnish on nickel sometimes are removed only by abrasive cleaners, and constant use of abrasives wears down the plating.

The behavior of nickel-plated steel sheet specimens in 18-months exposure has shown the important beneficial effect of increasing the thickness of the nickel layer. The tests were made in six different locations⁴ under the auspices of the American Society for Testing Materials, the American Electroplaters' Society, and the National Bureau of Standards. The data given in Table 211 derive from these tests. The higher the "score" the better the behavior.

It was concluded by the authors that for severe exposure the nickel plate on steel should be at least .01 in. in thickness, and for mild and indoor exposure at least .0005 in. thick.

With plates of .001 in. thickness, and less (thicker layers are at present unusual), the life of nickel plate in indoor exposures is numbered in years. In outdoor exposure behavior is less satisfactory; where the plate is cleaned occasionally, as in the case of automobile trim, behavior is reasonably good. In more corrosive conditions such as moisture-laden marine atmospheres and the sulfur-bearing atmospheres of cities the value of nickel-plated steel is rather doubtful. Where the plated object is subjected to immersion in water, salt solutions, acids, alkalies, and food products, nickel plating is but a temporary expedient.

TABLE 211.—*Nickel Plate vs. Atmosphere.*

	Score			
	.00025 in. nickel	.0005 in. nickel	.001 in. nickel	.002 in. nickel
Non-industrial				
State College, Pa.....	31	70	87	96
Washington, D. C.....	35	82	86	94
Industrial				
New York City.....	17	30	67	86
Pittsburgh, Pa.	8	20	36	52
Marine				
Key West, Fla.....	10	25	67	79
Sandy Hook, N. J.....	10	27	62	79

The “score” relates to the criterion of comparison, per cent of surface rusted, as follows:

Score	Per cent of surface rusted
100	0
80	0-5
60	5-10
40	10-20
20	20-50
0	50-100

STRESS-ACCELERATED CORROSION AND CORROSION FATIGUE

McAdam ²⁶⁻²⁹ has determined the damage suffered by cold-worked nickel from combined cyclic stress and corrosion by carbonate tap water, using change in fatigue strength as the measure of damage. The curves of Figure 52 represent, on the zero line, the damage resulting from stressless corrosion, and on the other lines the damage resulting from the correspond-

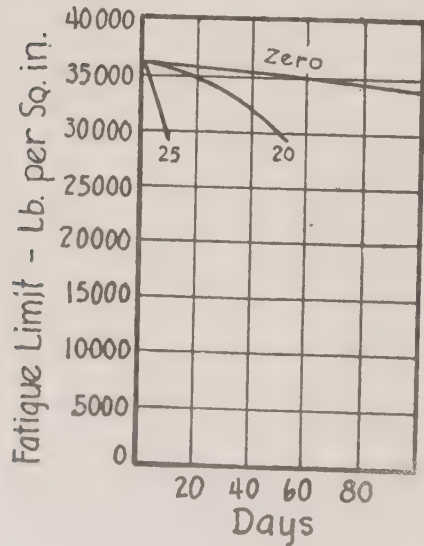


FIGURE 52. Nickel vs. Fresh Water in Fatigue.²⁷

ing combinations of stress and time in corrosion exposure. The ordinates are the resultant fatigue limits.

In Figure 53 are plotted the combinations of time, number and rate of cycles, and stress in corrosion exposure which damaged the metal to the extent of a 15% drop in the fatigue limit. The abscissae represent both time and average rate of net damage. Two curves are included of data of

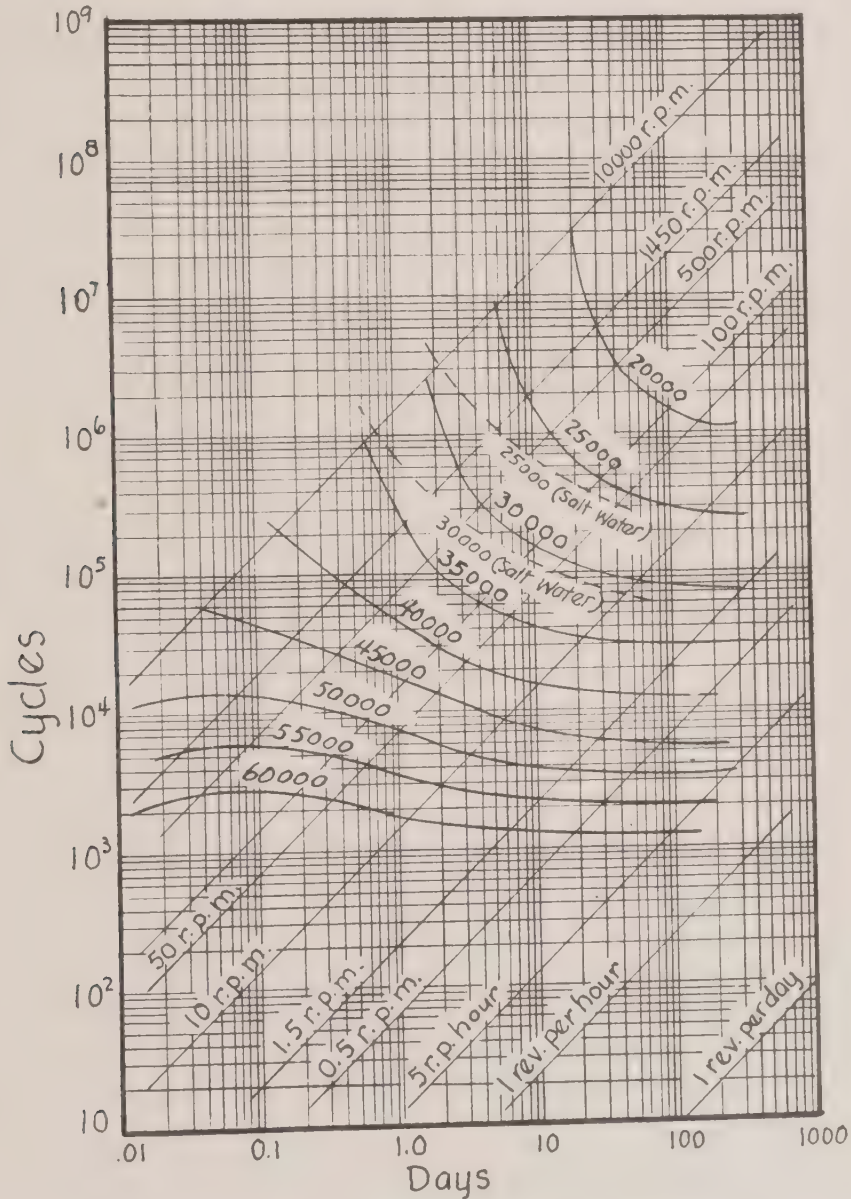


FIGURE 53. Nickel vs. Fresh Water in Fatigue.²⁷

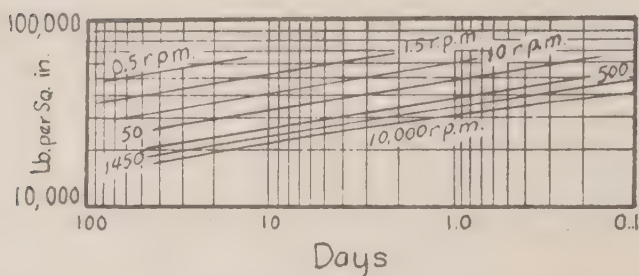


FIGURE 54. Nickel vs. Fresh Water in Fatigue.²⁷

tests in brackish sea water. This condition is more damaging by several times than tap water.

Finally, in Figure 54 the stress is plotted against time for different cycle frequencies to produce 15% damage. The damage represented in Figures 53 and 54 is purely corrosion-stress damage.

TWO-METAL GALVANIC BEHAVIOR

In electrochemical nature nickel is characteristically cathodic (protected) to iron and usually anodic (corroded) to copper. This generalization applies to the range of aqueous solutions against which the resistance of both nickel and the other metal is of a commercial nature. The susceptibility of nickel to passivation becomes perhaps a factor in its galvanic behavior, tending to make it less powerful as a cathode.

The coupling of aluminum with nickel is not good practice in any acid or salt solutions in which the two metals separately have good resistance. The use of aluminum paddles with a nickel milk pasteurizer, for instance, resulted in complete protection of the nickel and rapid corrosion of the paddles, the relative areas of nickel to aluminum being 5 to 1. The aluminum when not coupled with nickel was resistant to the point of being almost unattacked. Likewise in moist atmospheric exposure the coupling of these is to be avoided unless a very slight accelerated attack of the aluminum is allowable.

Nickel is normally cathodic to tin, lead, and zinc. In acid solutions these metals would tend to corrode at an accelerated rate, with the exception that with lead in sulfuric the insulating film of lead sulfate largely prevents the flow of galvanic current. In a boiling solution of 0.25% sulfuric acid and 0.15% nitric lead was anodic, by potential measurement, to nickel.²² In neutral reacting solutions couples of nickel with tin and lead and lead-tin solders are relatively safe.

Couples of nickel and iron lead to acceleration of the corrosion of iron. The acceleration is rather considerable in those dilute acid solutions with which cast iron is sometimes used. The data below²² illustrate the effect in 5% sulfuric acid at room temperature; the area of the iron was .14 sq. dm. and of the nickel 3.3 sq. dm. The corrosion rates are for iron.

Iron vs. Sulfuric Acid.

	Mg. per sq. dm. per day
Uncoupled	1,700
Coupled with nickel.....	19,600

The area relations in this case favored greater acceleration of the attack. The e.m.f. under the same conditions ranged at 0.37 to 0.47 volt.

In neutral solutions—brines, sea water—iron likewise tends to suffer in couple with nickel, the degree of action depending on aeration of the solution. Evans ¹¹ found an e.m.f. range up to 0.4 volt developing between steel and nickel in dilute salt solutions, tap water and distilled water. Nickel became temporarily anodic to steel in a single case where freshly abraded nickel was coupled in tap water with steel, the water against the steel being aerated. Acceleration of attack is indicated by the results of tests in Table 212 in which iron, both uncoupled and coupled with nickel, was partially immersed (plentiful oxygen supply) over a 14-day period. The electrodes were clamped 2.2 cm. apart.

TABLE 212.—*Iron vs. Water and Salt.*

	Weight Loss of Steel—Grams	
	1 N Sodium Chloride	Tap Water
Uncoupled	27	14
Coupled with nickel electrode areas equal	51	9
Cathode area twice that of anode area,	75	10

Copper coupled with iron in the salt solution caused a greater acceleration than the nickel, and lead a lesser. Using steel specimens sprayed with copper and with nickel, Evans ¹⁰ found copper to be a more intense accelerator than nickel, in partial immersion in one-half normal sodium chloride, and in tap water. In these tests the same volume of rust resulted whether the steel was uncoated or was coated with nickel in a discontinuous layer, a thin layer (.001 cm.), or a thick layer (.01 cm.).

Aeration is the greatest single factor in the corrosion of iron by neutral solutions; aeration likewise favors galvanic acceleration of iron when coupled with nickel. The data below ²² suggest the effect of nickel couples, these rates applying to fully aerated and agitated 3% sodium chloride at room temperature, with a cathode area of 3.3 sq. dm. and anode area of 0.14 sq. dm. The corrosion rates are for iron:

Iron vs. Salt.

	Mg. per sq. dm. per day
Uncoupled	350
Coupled with nickel.....	7,600

In alkaline solutions iron tends to be anodic to nickel, as indicated by the results of tests in caustic soda solutions in Table 213.²²

TABLE 213.—*Nickel : Iron Couples vs. Caustic Solutions.*

Conditions	Anode	Cathode	Volts
100°–130° Tw.; 26" vac.; 75 lbs. steam	Cast iron	Nickel	.15
	Ingot Iron	Nickel	.19
30° Tw.; 7" vac.; 8 lbs. steam.....	Cast iron	Nickel	.43
	Ingot iron	Nickel	.46

Further data on the potential difference in caustic were published by McKay.³¹

Nickel coupled with Monel metal, copper, the brasses, and the bronzes develops usually only small potential differences, on the order of .05 volt and less. Voltages of over 0.1 have been observed against a copper-nickel alloy, with nickel anodic, in agitated milk, yet in an aerated solution of lactic acid and sodium chloride nickel was anodic at 0.03 volts. The electrochemical nature of nickel and the copper alloys is so nearly alike that the direction of polarity between nickel and any other metal in the group may reverse under some conditions of aeration, agitation, polarization, and the solution itself. The results in Table 214 have been obtained ²² in agitated pasturized milk. The nickel silver carried 55% copper, 27% zinc, and 18% nickel; the copper-nickel alloy was a 70:29 composition with 1% tin.

TABLE 214.—*Nickel : Copper Alloy Couples vs. Milk.*

Temp. °F.	Time Hours	Anode	Cathode	Volts
86	0.0	Nickel	Copper-nickel	.049
	2.0	Nickel	Copper-nickel	.045
	3.5	Nickel	Copper-nickel	.045
145	0.3	Nickel	Copper-nickel	.082
	1.0	Nickel	Copper-nickel	.099
	1.2	Nickel	Copper-nickel	.13
	1.5	Nickel	Copper-nickel	.13
	2.0	Nickel	Copper-nickel	.13
86	0.0	Nickel	Nickel-silver	.053
	2.0	Nickel	Nickel-silver	.040
	3.5	Nickel	Nickel-silver	.036
	4.0	Nickel	Nickel-silver	.036

Tests in aerated, agitated 3% sodium chloride gave the data in Table 215.

TABLE 215.—*Nickel:Copper-Nickel Couples vs. Salt.*

Time—Hours	Anode	Cathode	Volts
0.0	Copper-nickel	Nickel	.054
0.33	Nickel	Copper-nickel	.0027
18	Copper-nickel	Nickel	.062

Another case of changing polarity is that of nickel coupled with a bronze casting (85% copper, with tin and lead) immersed in quiet tap water relatively high in chloride.²² (See Table 216.)

TABLE 216.—*Nickel : Bronze Couples vs. Water.*

Hours	Anode	Cathode	Volts
0	Nickel	Bronze	.063
5	Bronze	Nickel	.023
22	Bronze	Nickel	.056

That the coupling of nickel with copper metals may sometimes lead to appreciable accelerated attack is shown in data (Table 217) from tests in air-saturated and agitated sodium chloride.²² The brass was 70 Cu 29 Zn 1 Sn.

TABLE 217.—*Nickel : Brass Couples vs. Salt.*

	Area	Mg. per sq. dm. per day Coupled	Uncoupled
Brass	0.29 sq. dm.	108	18
Nickel	0.14 sq. dm.	0	1.9

The couple developed .058 volt at the start of the test and .11 volt after 16 hours, with brass the anode.

On the other hand couples of these metals may not lead to accelerated attack, as indicated by the results in Table 218²² of a nickel and copper couple in aerated, agitated 20% calcium chloride:

TABLE 218.—*Nickel : Copper Couples vs. Chloride.*

	Area	Mg. per sq. dm. per day Coupled	Uncoupled
Copper26 sq. dm.	103	152
Nickel26 sq. dm.	27	30

Presumably the accumulation of corrosion products or polarization by gas suppressed the galvanic effect.

Although experience has shown that the coupling of nickel with the metals of the copper group in exposure to waters, the atmosphere, steam, and neutral salt solutions is in most cases safe practice, it is well to avoid such couples in acid exposure unless the design will allow some accelerated action. In acid solutions nickel may act as cathode or anode to the other metal, depending on various factors such as aeration. In one case nickel coils held by copper straps, handling a hot mixture of sulfuric acid, water, ethyl alcohol, and calcium acetate were corroded through at the copper:nickel:solution contact. Except in this area the nickel was practically uncorroded; the affected area extended 3 inches each side of the straps, the straps being 5 inches wide.

Likewise, nickel suffered in contact with copper exposed in an esterification still, the solution consisting of acetic and sulfuric acids, water, and

alcohols at about 200° F. The specimens, 0.5 sq. dm. in area, were separated by and in electrical contact with a small nickel spacer, .018 sq. dm. in area.²¹ (See Table 219.)

TABLE 219.—*Nickel : Copper Couple vs. Hot Acid.*

	Mg. per sq. dm. per day	
	Coupled	Uncoupled
Copper specimen	68	416
Nickel spacer	1870	
Nickel specimen	960	500

On the other hand copper was anodic to nickel in air-saturated, agitated 5% sulfuric acid.²² (See Table 220.)

TABLE 220.—*Nickel: Copper Couple vs. Acid.*

Anode	Cathode	E. M. F., volts
Copper	Nickel	.050
Nickel	Monel Metal	.011

The chromium iron and the chromium-nickel iron alloys vary in polarity against nickel depending upon whether the alloy is in the passive or active state. In oxidizing acid or oxidizing salt solutions nickel is anodic and if the solution is corrosive to uncoupled nickel, acceleration would tend to result if coupled with a chromium alloy. An e.m.f. of 0.50 volts between nickel and 18-8 stainless steel, with nickel anodic, was developed in a boiling solution of .25% sulfuric and .15% nitric, the nitric acting to passify the alloy. A nickel and 18-8 couple in quiet sweet milk and buttermilk at 143° F., for instance, was free of accelerated action. On the other hand chromium alloys when cathodic are likely to accelerate the attack of an anode metal,⁵⁶ like nickel, much as platinum would.

ACID SOLUTIONS

Nickel has generally good resistance, much like copper and the copper alloys, against the non-oxidizing group of acids—sulfuric, hydrochloric, phosphoric, acetic, tartaric, and others. Aeration and higher temperatures are accelerating conditions; air-saturated solutions of these acids are characteristically strongly corrosive, and solutions at temperatures approaching boiling often are too corrosive to make the use of nickel practical. Against inherently oxidizing acids—nitric, sulfurous, acid and ferric salt mixtures, chromic acid at times—the resistance of nickel is not good.

Sulfuric acid. Though less resistant than lead or silicon iron or Monel Metal, nickel is sometimes used with sulfuric acid.^{5, 16, 17, 21, 22, 25, 30, 57} In dilute, unheated solutions of relatively low aeration the resistance of nickel is good; strongly aerated solutions, and boiling solutions are too

strongly corrosive to make the use of nickel practical. Corrosion is more rapid at intermediate than at low or moderately high concentrations. Concentrated (80 to 100%) acid in the cold is inclined to be seriously corrosive, and when hot is very corrosive. A general idea of behavior is afforded by the typical rates for different conditions in Table 221.

TABLE 221.—*Nickel vs. Sulfuric Acid.*

Condition	Mg. per sq. dm. per day
Cold, substantially air free, 1-80%	<10
Cold, quiet submersion, 1-80%	25
Cold, moderate aeration and agitation, 1-20%	100-300
Hot, 1-20%	300-500
Boiling, 1-20%	1,000
Boiling, 80-100%	40,000

Nitric acid. Attack of nickel by nitric acid is quite appreciable at low concentrations and increases very rapidly with concentration and temperature. Aeration is not necessary for attack, because of the oxidizing power of the acid. The intensity of corrosion is somewhat as follows:

Maximum (moderate to high concentrations)	50,000 mg. per sq. dm. per day
Average (dilute acid)	5,000 mg. per sq. dm. per day
Low (very dilute acid)	250 mg. per sq. dm. per day

Hydrochloric acid. Nickel is one of the better resistants against hydrochloric solutions,^{8, 14, 16, 17, 21, 30} yet this does not mean its resistance is of a high order, since hydrochloric is one of the most difficult of the acids to handle. From the practical standpoint, nickel may be considered resistant to hydrochloric solutions at room temperature up to around 15% concentration under conditions where the acid has a low air content, e. g. quiet submerged exposure. The acceleration of attack with increase of temperature, concentration—in the lower range—and aeration is very rapid. Under less than extraordinary conditions hydrochloric acid might penetrate an inch or more of nickel in a year (60,000 mg. per sq. dm. per day) and at the slower rates the penetration will be from 100 to 200 mg. per sq. dm. per day.

An approximation of test rates is given in Table 222.

TABLE 222.—*Nickel vs. Hydrochloric Acid.*

	Mg. per sq. dm. per day
Cold, quiet, 1-15%	20- 100
Cold, quiet, 15-36%	100- 400
Cold, aerated, 1-15%	100- 800
Cold, aerated, 15-36%	400- 2,000
Hot, 1-15%	500- 2,000
Hot, 15-36%	800-10,000

The effect of aeration in dilute acid exposure is indicated by the data in Table 223.¹⁴ The tests ran for 48 hours following 48-hours previous exposure, and were made at room temperature.

TABLE 223.—*Nickel vs. Hydrochloric Acid (1 N).*

	Mg. per sq. dm. per day
Total immersion	
Quiet	55
Air-agitated	174
Alternate immersion	
Continuous	900
Intermittent	380
Spray (4 to 30 days)	87

Phosphoric Acid. It is not ordinarily safe to use nickel with process phosphoric solutions,^{22, 24} carrying iron salts, as in the processing of acid from phosphate rock, since these are strongly corrosive to nickel. Thus at 176° F. a dilute solution of crude phosphoric, carrying 0.40% iron, corroded nickel at a rate of 5,000 mg. per sq. dm. per day with pitting.²⁴ In the absence of iron, phosphoric in the cold has low to moderate action on nickel, rates being on the order of 20 to 80 mg. per sq. dm. per day for quiet exposure, and 50 to 200 for agitated aerated acid. Hot concentrated solutions of pure acid are very corrosive, rates running above 1000 mg. per sq. dm. per day.

Acetic acid. Against acetic solutions ^{8, 14, 21, 22, 45, 57} of mild and low aeration, and of low concentrations (under 1%) whether aerated or not, the resistance of nickel is reasonably good. Temperature has an accelerating effect, but even boiling acid is resisted fairly well. In cold highly aerated acid the rates range around 300 mg. per sq. dm. per day and may be considered somewhat too high for continuous contact under most conditions. (See Table 224.)

TABLE 224.—*Nickel vs. Acetic Acid.*

	Mg. per sq. dm. per day
Cold, quiet, 1-100%	10- 50
Cold, moderately aerated, 1-100%	50-150
Cold, highly aerated and agitated, 1-100%	250-400
Hot, 1-100%	50-150

Below are data ¹⁴ covering the effect of aeration in cold dilute acetic acid solutions. The tests were made at room temperature, and ran for 48 hours, following previous 48-hours exposure. (See Table 225.)

TABLE 225.—*Nickel vs. 3% Acetic Acid.*

	Mg. per sq. dm. per day
Total immersion	
Quiet	23
Air agitated	143
Alternate immersion	
Continuous	155
Intermittent	68
Spray (4 to 30 days)	29

The results in Table 226 were obtained ²² in boiling acetic solutions, in 1 hour exposure, and illustrate the effect of dilution as a factor.

TABLE 226.—*Nickel vs. Boiling Acetic Acid.*

Acetic Conc. pH	Mg. per sq. dm. per day
4.3	230
5.3	120
6.0	60
6.75	<2

The results in Table 227 were obtained in tests in which the specimens were held either submerged in boiling acid, or exposed to the vapors of the boiling acid. The duration was 20 hours.²²

TABLE 227.—*Nickel vs. Boiling Acetic Acid.*

Acetic %	Mg. per sq. dm. per day	
	Submerged	In Vapors
5	66	46
50	116	90
98	74	24
99.9	85	14

Similar tests were made in acid and anhydride mixtures. (See Table 228.)

TABLE 228.—*Nickel vs. Acetic Acid and Anhydride.*

Solution		Mg. per sq. dm. per day	
Acid %	Anhydride %	Submerged	In Vapors
30	70	144	213
2	98	26	34

Organic acids other than acetic. The hydroxy-acids are roughly alike in their action on nickel.^{8, 21, 22, 25, 35} The differences observed in tests do not lend themselves to generalization. As a group these acids are well resisted by nickel when aeration is low to moderately high. With very high degrees of aeration, or in boiling acid, the attack is inclined to be fairly rapid, particularly with the higher concentrations of hydrogen ion. Approximation of rates is given in Table 229.

TABLE 229.—*Nickel vs. Organic Acids.*

	Mg. per sq. dm. per day
Cold, quiet, all concentrations	1-20
Cold, aerated, moderate (most corrosive) concentrations..	20-100
Hot, all concentrations	50-300

A set of data ⁸ that is useful in that several acids and conditions are covered is given in Table 230. Aeration was of low order. The cold tests ran for 5 days, the hot for 20 hours.

TABLE 230.—*Nickel vs. Organic Acids.*

Acid	Mg. per sq. dm. per day		pH = 2 212° F
	0.1 N Room Temp.	0.1 N 212° F.	
Formic		45	40
Lactic	3.5	56	75
Tartaric	2.2	93	310
Malic		40	25
Acetic	2.8	43	53
Citric	4.9	56	93

Oxidizing substances in acid solutions. Oxidizing substances like ferric salts and copper salts, peroxide, chromates in acid solutions are inclined to be very corrosive to nickel. Data on some of these are given below. Very low rates were obtained in some cases, due to passivation, yet this high degree of resistance under such conditions cannot normally be expected.

Nickel specimens, exposed to flowing acid mine water for 98-135 days, at atmospheric temperature, gave the rates in Table 231.⁴⁷ Nickel is not useful with these, nor for that matter with any acid solutions carrying ferric iron.

TABLE 231.—*Nickel vs. Oxidizing Acid.*

Conc. %		Mg. per sq. dm. per day
Sulfuric	Ferric Iron	
.14	.006	146
.22	.09	.3
.043	.014	118

A 6% sulfuric solution carrying .85% dissolved copper corroded nickel at a rate of 400 mg. per sq. dm. per day in a 24 hour room temperature test.²² Nickel generally should not be used with acid solutions carrying copper.

A mixture of 0.9% sulfuric and 27% chromic acid corroded nickel at the rates in Table 232.²² Chromic acid is too strongly oxidizing to nickel to allow the latter's use. Pure nickel in this case was passive, but passivity cannot be depended upon.

TABLE 232.—*Nickel vs. Oxidizing Acid.*

	Mg. per sq. dm. per day	
	120° F.	80° F.
Nickel, pure	0	0
Nickel, 2% manganese	4780	4300
Nickel, 5% manganese	236	3160

Sulfidizing substances in acid solutions. Sulfurous acid and hydrogen sulfide in solution attack nickel strongly with the development of sulfide corrosion products and pitting. Rates in sulfurous acid^{8; 22} run as high as 500 to 1000 mg. per sq. dm. per day. In acid solutions carrying sulfide, such as hydrogen sulfide in solution corrosion may not be so severe, yet action is too intense to make nickel useful.

ALKALINE SOLUTIONS

Caustic solutions. Nickel is an extremely good resistant to caustic alkaline solutions,^{14, 16, 21, 22, 25, 30, 31} such as sodium and potassium hydroxide and sodium carbonate and bicarbonate. Rates run ordinarily below 1 mg. per sq. dm. per day in any concentration, cold and hot, with the exception that very hot concentrated solutions may at times run rates up to 10 mg. per sq. dm. per day.

A one-normal solution of sodium hydroxide at room temperature gave rates as in Table 233.¹⁴ The tests ran 48 hours following 48-hours previous exposure.

TABLE 233.—*Nickel vs. Sodium Hydroxide (1 N).*

	Mg. per sq. dm. per day
Total immersion	
Quiet4
Air-agitated	<.1
Alternate immersion	
Continuous	3.1
Intermittent	3.7
Spray (4 to 30 days)4

Tubes of caustic evaporators are commonly made of nickel, both because of its resistance and the fact that nickel in the quantities absorbed by the caustic is not considered injurious.³¹ Welded nickel tubing for 20 months in an evaporator operating at an average temperature of 203° F. and delivering 50% caustic showed, on visual inspection, no penetration from the caustic. In another case welded nickel tubing after 4½ years in an evaporator handling caustic at about 194° F. had thinned on the caustic side only just appreciably. Galvanic corrosion of cast iron or steel tube sheets is likely to result through contact with nickel tubes, the corrosion tending to be greater in caustic of higher temperatures and concentrations. Corrosion rate data in hot caustic are given below:

Caustic soda concentrating from 32 to 52% ; 5½ hours ; 196° F.³¹—8 mg. per sq. dm. per day.

Caustic soda concentrating from 30 to 50% ; specimens suspended in liquor of the downtake of a single effect caustic evaporator ; 179° F. ; 380 hours ³¹— .6 mg. per sq. dm. per day.

Pure concentrated caustic at 200° F. ; 20 hours ; agitated ²²—1 mg. per sq. dm. per day.

Pure concentrated caustic with 0.3% sulfate and 0.3% chloride added, and saturated in iron ; 20 hours ; agitated ; 200° F.²²—6 mg. per sq. dm. per day.

Aqueous ammonia. Dilute ammonium hydroxide is well resisted by nickel, whereas concentrated solutions are likely to be corrosive particularly if aerated. The division point between concentrations that are strongly corrosive to nickel and those against which nickel is relatively passive shifts with aeration, iron content of the nickel, and impurities in the ammonia. An approximation of rates is given below :

Nickel vs. Aqueous Ammonia.

	Mg. per sq. dm. per day
Concentrated and aerated solutions	3000
Dilute solutions	5

Anhydrous ammonia has no action on nickel.

The rates in Table 234 were obtained in room temperature tests that ran 48 hours following previous 48-hours exposure.¹⁴ The solution was a one-normal concentration.

TABLE 234.—*Nickel vs. Aqueous Ammonia.*

	Mg. per sq. dm. per day
Total immersion	
Quiet	5
Air-agitated6
Alternate immersion	
Continuous	17
Intermittent	2.5
Spray (4 to 30 days)	<.1

These rates and those in Table 235 illustrate the good resistance of nickel in the lower concentration range of solution. The data in Table 235 were obtained in a 10% solution over a 50-hour test period.²⁵

TABLE 235.—*Nickel vs. 10% Aqueous Ammonia.*

	Mg. per sq. dm. per day
Un aerated	1.8
Aerated	2.2

In contrast with the negligible action represented in the data in Table 235, the high rates in Table 236 are typical of the greater concentration

range of solution. These tests were made in highly agitated ammonium hydroxide at room temperature, over a 20-hour period.²²

TABLE 236.—*Nickel vs. Aqueous Ammonia.*

Conc. % Ammonia	Mg. per sq. dm. per day
1.1	0
12.9	3,500
20.2	2,300
27.1	1,100

Under quiet exposure conditions, in 6-hour tests, the rates in Table 237 were obtained.²²

TABLE 237.—*Nickel vs. Aqueous Ammonia.*

Conc. % Ammonia	Mg. per sq. dm. per day
12	445
28	210

SALT SOLUTIONS

Non-oxidizing salt solutions.^{14, 16, 20, 22, 25, 42, 43} Nickel has a high degree of resistance against solutions of the alkaline and alkaline earth and related salts, such as the chlorides, carbonates, sulfates, nitrates of sodium, calcium, zinc. At times in wet and dry exposure, action though slight results in accumulations of thin green corrosion products and, very rarely, in fine pitting.

An approximation of rates is as follows:

	Mg. per sq. dm. per day
Cold, quiet exposure, of all solutions of this type.....	<1
Cold and hot, and moderately aerated, agitated, all salts..	<1-10
Cold, strongly aerated and agitated, chloride brines.....	10-30

The rates in Table 238 for nickel are typical of action of this group of salts in solution. The tests¹⁴ were made at room temperature, and ran 48 hours following a previous 48-hours exposure.

TABLE 238.—*Nickel vs. Salt Solutions.*

	Mg. per sq. dm. per day 1 N Sodium Chloride	1 N Potassium dichromate
Total immersion		
Quiet	1.9	1.
Air-agitated	1.7	.6
Alternate immersion		
Continuous	2.5	2.0
Intermittent	4.4	1.
Spray (4 to 30 days)	<.1	<.1

Oxidizing salt solutions—acid. Solutions of salts of the heavy metals, like ferric chloride, mercuric chloride, copper chloride, stannic chloride and silver nitrate are acid in character and strongly oxidizing in relation to nickel. As a result the action of these on nickel is moderate to strong, and generally speaking, other metals or substances than nickel are more suitable for handling them. In some cases—copper salts and silver salts—the heavy metal plates on the nickel in an uneven layer that results in pitting attack. In the case of stannic and ferric salts, action is inclined to be very rapid.

Corrosion rates for this group range around 60 to 300 mg. per sq. dm. per day, sometimes higher, with the added danger of pitting.

Oxidizing salt solutions—alkaline. Hypochlorite solutions, except in very dilute concentrations, are corrosive to nickel. The more concentrated solutions—above about 0.3% available chlorine (3 grams per liter)—corrode with rapid pitting, and in the case of more dilute solutions it is better not to use nickel where continuous exposure is required.

Sulfidizing salt solutions. Solutions of sodium sulfide react with nickel to form a black sulfide layer on the metal. This film tends both to prevent general corrosion and to set up pitting action. Submerged in 1.5% sodium sulfide carrying 0.1% sodium carbonate, aerated with hydrogen sulfide, at 147° F., nickel was corroded at a rate of 54 mg. per sq. dm. per day. Specimens exposed in the vapors of moisture, air, hydrogen sulfide at 150° F. were attacked at a rate of 160 mg. per sq. dm. per day. At 105° F. the rate was 23 mg. per sq. dm. per day.²²

ATMOSPHERE

Nickel plate and, to a less extent, solid nickel are commonly used for appearance in atmospheric exposure. Indoors the tendency for the metal to tarnish or acquire a film is slight, less so than in the case of copper and brass and in many cases silver, but more so than with chromium-plate; with more or less regular cleaning good appearance may be maintained. In outdoor exposure nickel becomes much more rapidly dulled and tends to acquire a superficial loosely adherent greenish to white corrosion product. The actual penetration rate is low in non-industrial atmospheres, somewhat greater in atmospheres carrying sulfur in relatively large quantities. Based on the evidence of Hudson's tests¹⁹ covering exposure of a year, the resistance of nickel to actual penetration is not unlike that of copper in rural and sea-coast atmospheres, somewhat less than that of copper in urban atmospheres.

Vernon⁵³ has said, after a great deal of investigation: "The behavior of nickel, on exposure to the atmosphere, is sharply differentiated from that

of the other metals in common use. We are all familiar with the characteristic creamy film which sooner or later makes its appearance on articles of nickel or nickel-plate. In the early stages the film can be removed quite easily, merely by wiping with a cloth; very soon, however, more vigorous treatment is needed in order to effect its removal, and at a later stage the film cannot be removed at all without abrading the underlying metal. The phenomenon is quite distinct from tarnishing, as hitherto understood: for convenience we may refer to it as "filming" or "fogging." The effect is undoubtedly the more pernicious one, since it quickly detracts from the brilliant luster, which, together with its hardness and durability, renders nickel so valuable as a protective and decorative covering. There can be little doubt, indeed, that in the absence of this defect the need for more troublesome and more expensive chromium plate would not have arisen. What happens at first is apparently a physical condensation on the metal surface, followed by a chemical reaction between the deposited film and the underlying metal. We know that atmospheric humidity plays an important part in the initial condensation, for if the temperature is maintained sufficiently above the dew-point the metal remains bright indefinitely, even though other factors are favorable; on the other hand it is not necessary for the dew-point to be reached, and indeed filming may occur when the content of water vapor in the atmosphere is only some 70% of that required for saturation. There are also good reasons for believing that sulfur compounds again play an essential part: not sulfides, however, as in tarnishing (i. e. H_2S or compounds which give a similar chemical reaction) but oxides (i. e. SO_2 and SO_3). Thus analysis of the film after prolonged exposure shows that it consists essentially of basic *sulfate*, in contrast with the *oxysulfide* which constitutes the tarnish* films previously considered. It is of interest to note, moreover, that whereas a relatively high humidity is necessary for fogging, tarnishing proceeds most rapidly when the relative humidity is low."

Vernon also has called attention to the possibilities of lacquers, vaseline and lanoline as preventives of filming.

In exposure tests lasting a year, Hudson¹⁹ obtained the penetration rates in Table 239 for nickel exposed a year in various atmospheres, deriving the rates from three different criteria of behavior. The fact that the electrical resistance method yielded the greatest penetration rates suggests that attack was not entirely a smooth one. The most important fact these results bring out is the low order of attack by the various atmospheres. The greater corrosiveness of the urban atmosphere is obvious. Specimens giving the loss-in-weight and change in resistance data were exposed freely to the wash of rain, the weight-increment specimens were protected.

* The tarnish referred to is characteristic of copper and copper alloys.

TABLE 239.—*Nickel vs. Atmosphere.*

Atmosphere	Mg. per sq. dm. per day		
	Weight Increment Method	Elect. Resistance Method	Loss in Weight Method
Rural4	1.0	.3
Suburban6	1.7	.6
Mild industrial	1.4	3.5	1.36
Urban	1.5	3.5	1.42
Marine9	2.0	.7

The deliquescence of corrosion products is a factor in the resistance of metals in the atmosphere. Hudson found that the corrosion product that developed on nickel, in exposure to an urban atmosphere though protected from the wash of rain, was more markedly deliquescent than that developed on aluminum, copper, or iron. Hudson has stated "materials that form very deliquescent corrosion products will, in general, tend to suffer more corrosion than those that do not."

Nickel window screen exposed ²² to the weather and sun for 18 months on the New Jersey seacoast acquired a dull brown, thin, hard, finely granular product; beneath this the metal was "frosted" with no evidence of pitting or increased attack at intersections. In contrast, nickel screen exposed in Pittsburgh rapidly darkened and after the first rain a slight scattered deposit of green crystals appeared. By the end of somewhat over a year the metal was uniformly pitted to a depth of .002 inch, which corresponds to a maximum corrosion rate of 12 mg. per sq. dm. per day in the pits.

WATERS

In exposure to natural waters, sea water, distilled water, etc., the attack on nickel is for the most part slight or non-existent. When constantly immersed in waters, nickel remains bright and clean; in wet and dry exposure, particularly if the salt content of the water is relatively high (sea water) and in humid atmosphere green salts in time are likely to accumulate, absorb moisture and tend to produce localized corrosion.

Contamination from metal absorption is the important point when considering distilled water. Calculations from analyses of water drawn from a small size laboratory nickel storage tank showed the water to absorb on the order of 0.01 parts nickel per million, based on the assumption that the water is entirely renewed every two days. The absorption rate was determined to be .006 mg. per sq. dm. per day; subsequent tests with the same apparatus gave even lower rates than this.²²

Some experience with condenser tubes has indicated that pure nickel tubes are not so satisfactory for turbine condenser installations handling sea

water velocities on the order of 8 ft. per sec. as might be expected from the properties of high nickel-copper alloys. The drawback of nickel in this service lies in its tendency to pit, the pitting originating mostly in metal-lurgically defective fissured areas in the surface of the tube, but in cases also where defects are not recognizable.

Exposed 4 years in the sea water of Bristol (England) Channel at such a location that the metal was submerged 93% of the time, a bar of nickel was corroded at the rate of 1.9 mg. per sq. dm. per day. Incipient, very fine pitting of the surface had taken place over the 4-year period.¹³

The action on nickel of waters saturated with carbon dioxide is inclined to be much more corrosive than ordinary waters, although strangely enough passivity at times has been observed. Nickel wires exposed to tap water and distilled water, respectively, saturated with a mixture of carbon dioxide and oxygen for successive 20-hour periods without intermediate removal of the corrosion product gave the rates in Table 240.²²

TABLE 240.—*Nickel vs. Gas Saturated Water.*

Period in hours	Mg. per sq. dm. per day	
	Gas saturated tap water	Gas saturated distilled water
0- 20	27.8	21.1
20- 40	16.3	4.9
40- 60	+	3.3
60- 80	39.2	+
80-100	68.7	0.0
100-120	94.8	0.0

The extreme variability of rates is notable. Other tests were made, with weighing at the end of each 20-hour period, in distilled water saturated with air and carbon dioxide. In one series specimens were cleaned at the end of each series, in the other specimens were not cleaned. Here again rates were variable. (See Table 241.)

TABLE 241.—*Nickel vs. Gas Saturated Water.*

Period in hours	Mg. per sq. dm. per day	
	Product undisturbed	Product removed
0- 20	40.7	55.3
20- 40	76.5	45.3
40- 60	74.8	71.5
60- 80	85.5	120.3
80-100	212.6	128.5

Thus waters saturated with both carbon dioxide and air, an unusual set of conditions, are strongly corrosive. Ordinary carbonated water on the other hand is only faintly corrosive; a nickel-lined carbonator was filled with carbonated water and allowed to stand 10 days at room temperature under pressure of 200 lbs. per sq. in., with a resulting corrosion rate of 1.2 mg. per sq. dm. per day.³²

STEAM

Steam is very slow, often undeterminably slow, in its attack on nickel. Turbine blading of nickel is used in handling wet and dry steam, usually at high rates of movement, and at various temperatures and pressures. Steam-heating coils of nickel are in common use. It has been pointed out³¹ that impurities, notably carbon dioxide, may be present in steam and may result in appreciable corrosion on the steam side; "there is evidence that a small amount of corrosion may occur on nickel evaporators (caustic) from the steam, or rather from impurities in it. . . . In one case a penetration of 0.025 mm. in two years has been noted, and in another, a penetration of 0.23 mm. in 4½ years (12 mg. per sq. dm. per day). The latter was a welded tube and there was rather serious corrosion at weak points of the weld." In another case²¹ an average corrosion rate of 6 mg. per sq. dm. per day was observed in the case of nickel evaporator tubing handling steam at 284° F. and 90 to 135 lbs. pressure.

In steam in the range of temperature above 800° F. an embrittling action on nickel has been observed.⁶ In one case, during a 22-day period in superheated steam at 850° F., .035 inch nickel sheet was almost completely penetrated by this action. On the other hand delicate microscopic examination failed to reveal signs of embrittlement of nickel exposed 7 days at 760° to 780° F.²²

FOOD PRODUCTS

Nickel is extensively used for food-processing and food-handling equipment, since its corrosion resistance is high and the nickel salts absorbed by the foodstuffs are physiologically harmless. Dairy equipment, processing kettles, kitchen utensils and kettles, heating coils and fittings are common examples of nickel construction. Exposure to some products leads to discoloration of the metal and discoloration of the food. The latter may be unsightly but does not signify toxic contamination nor serious corrosion; it occurs characteristically in the cooking of cereals and grain foods if the time of contact is sufficiently long—e. g. 8 hours and longer.

Physiological effect. Nickel is classed as one of the non-toxic metals. The metal is a normal constituent of many raw foods and investigations have led to the conclusion that the metal absorbed by foodstuffs prepared in nickel equipment is harmless.^{7, 12, 32} After a careful review of existing data on the question of possible toxicity of nickel compounds, and investigations of their own, Drinker and co-workers⁷ have stated "the authors are consequently in agreement with the large group of foreign investigators who have found that the preparation of food in nickel utensils is entirely safe." There is in the conclusions of Bertrand² a suggestion that nickel may have a beneficial physiological function.

Fruit and vegetable juices. Fruit and vegetable juices,^{3, 8, 22, 35} acid in character, are ordinarily weaker in corrosive action on nickel than the corresponding concentration of pure acid. These juices are often handled by nickel. Aeration and elevated temperatures normally are accelerating factors, as in the case of the acids. In considering the suitability of nickel from the standpoint of change in the taste or appearance of the juice, it is well to keep in mind the relation between exposed metal area and the volume of solution, and also the expected time of contact between solution and metal. With a given product a large nickel container may be suitable where a small one is not; and continuous exposure of a few hours only may be permissible where storage for several days may not. Boiling fruit juices give corrosion rates of about 50 to 100 mg. per sq. dm. per day; rates in cold acid products range around 10 to 50 mg. per sq. dm. per day, with aeration somewhat accelerating.

For purposes of illustration several sets of data will be recorded here. Foodstuffs held at room temperature for 30 days gave the rates in Table 242 with nickel.⁸

TABLE 242.—*Nickel vs. Foodstuffs.*

	Mg. per sq. dm. per day
Cranberries	2
Preserves2-.5
Jams06-1
Currant juice	7
Tomato juice	1.7
Spinach	1
Vinegar	25

White grape juice with a .45% tartaric acid content gave the rates in Table 243 in 24 hours exposure.³⁵

TABLE 243.—*Nickel vs. Grape Juice.*

	Mg. per sq. dm. per day	
	Un aerated	Aerated
Room temperature	63	78
Boiling	190	62

Twenty-four-hour tests in other acid products at boiling temperature gave the results in Table 244.

TABLE 244.—*Nickel vs. Juices.*

	Mg. per sq. dm. per day
Tomato juice (.48% citric)	29
Apple juice (.28% malic)	26
Lemon juice (5.2% citric)	83
Red grape juice (.75% tartaric)	44

Nickel in quiet exposure in acid products held just below the boiling point gave the results in Table 245.⁸

TABLE 245.—*Nickel vs. Juices.*

	Mg. per sq. dm. per day
Tomato juice	14
Cranberry juice	50
Currant pulp	51
Raspberry syrup	32

Milk. Nickel is widely used for milk-handling equipment. It is possible from the data available^{15, 21, 32, 41, 51} to outline fairly specifically the factors affecting the behavior of nickel. The amounts of metal dissolved, from properly used nickel apparatus, by sweet milk are too small to have harmful physiological influence on the consumers of dairy products, and the quality of the products is not affected injuriously. In commercial pasteurization and storage of sweet milk in nickel equipment a possible maximum of 12 parts per million of nickel is absorbed. This value is greater than has actually been found in sweet milk that has been processed almost entirely in nickel apparatus³²—1.0 to 1.5 parts per million. Absorption quantities for buttermilk are somewhat higher.

At room temperatures and lower the corrosion rate of nickel in milk is low. In milk held at pasteurizing temperature or in milk being heated to pasteurizing temperature rates are likewise low. Under either of these latter temperature conditions a protective film is developed, aeration and flow both favoring its formation. On the other hand when milk is cooling from pasteurizing temperature the rates are relatively high; under cooling conditions in the temperature range of about 65-145° F. the action is too great to make the use of nickel feasible. As cooling progresses below this temperature range the action becomes less and less, at bottling temperature being negligible. An approximation of test results is given in Table 246.

TABLE 246.—*Nickel vs. Milk.*

	Mg. per sq. dm. per day
Room and storage temperature	0- 15
Heating and pasteurizing temperature	0- 50
Holding at pasteurizing temperature	48- 80
Cooling through range of 145 to 65° F. depending on rate of flow and aeration, both of which tend to accelerate corrosion	1200-100
Cooling through range of 65 to 40° F.	100- 0

HIGH-TEMPERATURE ATMOSPHERES

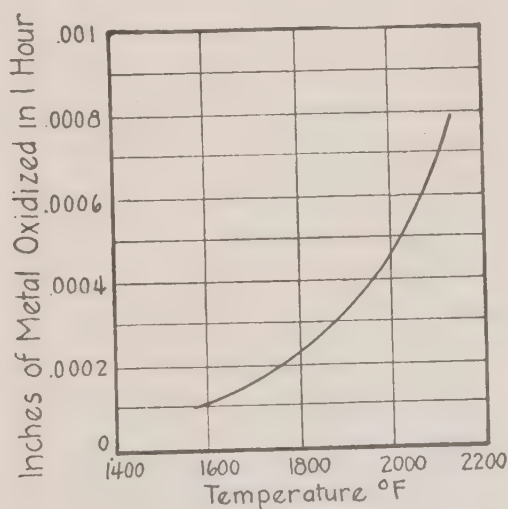
Nickel is in a sense a high-temperature metal.⁶ It has not the resistance of the nickel-chromium, chromium-nickel-iron and chromium-iron alloys in

the high temperature range, yet is much better in oxidation resistance than ordinary steels and any of the copper alloys. The presence of sulfur in hot atmospheres is very harmful to nickel, resulting in intergranular deterioration; sulfur compounds in a reducing atmosphere are even more reactive in this respect and active at lower temperatures than in an oxidizing atmosphere.

Oxidizing atmosphere. Nickel acquires in oxidizing atmospheres at elevated temperatures a tightly adherent brown coating of oxide, the thickness of which is dependent on the time and temperature of exposure and particularly on the protection the oxide affords against progressive oxidation. The minimum temperature at which the oxide begins to be visible is somewhere in the neighborhood of 600° F. The coating developed in lower ranges of heat seems to be protective, in the sense that progressive attack, or scaling, is either entirely prevented or is retarded sufficiently that for commercial purposes the metal may be employed up to temperatures of 1500° to 1600° F. for indefinite periods without rapid deterioration. Above this general range the oxide is likely to scale off and attack to be relatively rapid, though there are cases where nickel trays have been used with satisfaction for a great many hours to hold high speed tools during heat treating at temperatures up to 2250° F. Such trays are required only to remain capable of holding the tools, and surface deterioration and checking are not *per se* harmful.

In Figure 55 are shown oxidation rates of nickel at different temperatures based on a one-hour exposure period.³⁹

FIGURE 55. Oxidation Rate of Nickel in a One Hour Exposure Period.



The rate of oxidation is governed by the diffusion rate of oxygen dissolved in the oxide scale;^{38, 39} the square of the amount of oxidation is pro-

portional to the time of exposure. Thus the rates given in the diagram are not constant rates but merely the average rate in the first hour of exposure.

Poste⁴⁰ found an oxidation rate of 1800 mg. per sq. dm. per day for nickel heated in the atmosphere of a reasonably tight muffle at 1700° to 1800° F.; during the 215-hour exposure the metal was withdrawn several times, cooled and pounded lightly with a hammer. These conditions favored a high rate. Hatfield¹⁸ has recorded the gain in weight of nickel in 24-hours exposure in complex gases at 1650° F. The data are given in Tables 247 and 248.

TABLE 247.—*Content of Gas—Per Cent.*

Content of Gas—Per Cent	Complex Gas	Unenclosed Gas Muffle
Nitrogen	73	67.7
Oxygen	5	1.34
Carbon dioxide	12	4.75
Carbon monoxide		5.10
Steam	10	21.10
Sulfur dioxide05	.003

TABLE 248.—*Nickel vs. Gases at 1650° F.—Weight Increase.*

	Mg. per sq. dm. per day
Complex gas	520
Muffle gas	1680

Assuming the weight of metal oxidized to be approximately twice the weight of oxygen in the oxide—which for rough purposes is reasonably accurate—the deterioration rates would be 1000 and 3400 mg. per sq. dm. per day respectively. With longer periods of exposure the action would undoubtedly have been less, in view of the fact that the oxide becomes increasingly protective as it thickens.

Still further rates are given below.²² The nickel was exposed 15 days in a resistance furnace to an air current during the day and quiet furnace atmosphere at night:

° F.	Mg. per sq. dm. per day	
	Low Manganese Nickel	4% Manganese Nickel
1470	<74	<74
1650	74	1200
1830	6100	1500

Alternating oxidizing and reducing atmosphere. Under conditions in which the furnace atmosphere may alternate to be at one time oxidizing and at another reducing, an accelerated type of attack is apt to take place on nickel. Whereas the oxide formed by a consistently oxidizing gas is protective, this oxide is not stable against a reducing gas. Alternating gas conditions therefore result in successive formation and reduction of oxide,

and consequent relatively high degree of attack. This has been observed at 1300° F. and at a temperature as low as 900° F.^{6, 22}

Reducing gases carrying hydrogen and nitrogen. Vanick⁵² in investigating the effect of synthesizing ammonia atmospheres on metals, found a nickel tube of .35 inch wall to fail in 11 days by intergranular fissuring at 930° F.; the atmosphere was under 1500 lbs. pressure and the metal under 4000 lbs. per sq. in. initial stress. A nickel rod under similar conditions, except that the rod was not under stress, was penetrated through its 0.17-inch diameter in 14 days. The gas in each case was a mixture of nitrogen, hydrogen, and ammonia. In contact with cracking ammonia at 930° to 1112° F. nickel suffered severe fissuring.

The use of nickel is common in the construction of nitriding furnaces, in which the metal is exposed at temperatures of 900° to 1000° F. The resistance of nickel to the ammonia and to the gases resulting from the cracking is good, but some doubt exists that nickel is suitable for contact with gas that is actually being cracked.^{33, 34, 48, 55}

Sulfidizing gases. The presence of sulfur compounds in high-temperature atmospheres is extremely detrimental to nickel. This applies to oxidizing atmospheres, where the compound may be sulfur dioxide or trioxide, and particularly to reducing atmospheres where hydrogen sulfide or other reduced sulfur compounds may be present. The sulfidizing of nickel is in the nature of intercrystalline embrittlement. Nickel forms a eutectic series of alloys with the nickel sulfide Ni_3S_4 , the eutectic temperature being 1191° F.²³ In the heating of nickel for annealing, for subsequent hot-working operations, or in welding, precaution must be taken against the presence of sulfur compounds in the heating atmosphere. Sulfidization has resulted through the presence of sulfur from other sources than the atmosphere itself. Thus the marking of nickel with sulfurous chalk has resulted, on subsequent heating, in cracking. Heating nickel wire embedded in asbestos or kieselguhr carrying sulfur compounds has led to embrittlement. A nickel sheet facing a rubber roll over which cellophane passed from a precipitating tank became superficially sulfidized by the action of an intermediate compound, a thiocarbonate; subsequently the heat of silver soldering caused intergranular disintegration. Contact, therefore, with substances containing sulfur compounds decomposable by heat must be avoided.

Rates of attack of 30,000 mg. per sq. dm. per day and higher have been obtained in reducing gases carrying sulfur compounds at 1200° to 1300° F.²²

The action of hydrogen sulfide on nickel is strong even at relatively low temperatures. After an hour's exposure to hydrogen sulfide at 750° F. a scale of notable thickness could be peeled off.²³

In oxidizing gases carrying sulfur (sulfur dioxide) there is likewise a tendency towards sulfidizing embrittlement. Koster²³ thus found nickel sheet annealed one hour in sulfur dioxide at 1100° F. to crack in subsequent bending, whereas hydrogen treatment at a higher temperature left the metal ductile. Hatfield's tests¹⁸ indicate that the action of sulfur dioxide on nickel does not necessarily increase with temperature in a 24-hour exposure to the pure gas. (See Table 249.)

TABLE 249.—*Nickel vs. Hot Sulfur Dioxide.*

Temperature ° F.	Gain in weight of nickel Mg. per sq. dm. per day
1290	9,200
1470	36,600
1650	8,400
1830	260

What constitutes an undesirable rate or degree of deterioration from high-temperature exposure varies with every application. For instance, it may seem surprising that cast nickel rabble shoes are being used satisfactorily at 1100° to 1800° F. in the oxidizing and high sulfur atmosphere of an ore-roasting furnace.⁶ The life of these shoes runs around nine months. Under the partial pressure conditions within these furnaces the oxidizing reaction is predominant over the sulfidizing.

MISCELLANEOUS SUBSTANCES

Molten metals. Experience with mercury has indicated that the tendency of nickel surfaces to amalgamate is very slight and usually absent at ordinary temperature. At 700° to 800° F. amalgamation is pronounced. Like other metals, nickel for use with mercury should be in the annealed condition in order to avoid embrittling penetration.

With the exception of mercury the low melting point metals attack nickel more or less rapidly. Thus molten tin, lead, aluminum, zinc are moderately to strongly destructive. Nickel tubing has been eaten away quickly by molten tin at 450° to 500° F. Nickel immersed 14 days in molten lead was strongly corroded at the "water-line." Nickel dipped for 24 hours in molten zinc at 820° to 960° F. was corroded at an average rate of 1200 mg. per sq. dm. per day.²²

Fused compounds. Nickel is widely used in handling caustic fusions, particularly in laboratory work.^{9, 54} The use of nickel caustic pots is not practical if the caustic carries sulfur, the latter causing rapid attack. Muehlberg³⁶ considers fusion of ferro-silicon, chrome ore and other difficultly fusible substances, with sodium peroxide to be sound if the nickel crucible rests in water and the mixture, with sugar carbon, ignited directly.

Among the fused substances that attack nickel relatively rapidly are silver chloride, potassium bisulfate, vanadic oxide, borax, and as a rule cyanide.

Sulfidizing substances. Reduced sulfur compounds, both inorganic and organic, have a relatively strong tendency to react with nickel. Sometimes the reaction stops after the formation of a tarnish or black coating, in other cases pitting goes on beneath such a coating, and still again the action is relatively rapid. Molten sulfur eats nickel away with dispatch. Some naptha solutions of sulfides—hydrogen sulfide, mercaptan—in distilled water tarnished nickel, other substances did not over a 30-day period.⁵⁹ Sulfur-bearing petroleum products at elevated temperatures are corrosive. Thus a corrosion rate of 116 mg. per sq. dm. per day resulted from 75-days exposure of nickel in the first tower of a crude still.⁵⁸ At room temperature petroleum products carrying sulfur compounds and moisture may cause pitting.²² The average rates in Table 250 were obtained on nickel immersed in quiet petroleum products for 55 days at room temperature.

TABLE 250.—*Nickel vs Petroleum Products.*

	Mg. per sq. dm. per day	
	Submerged	In Vapors
Crude light oil	+	+
Neutral light oil04	.04
Motor benzol	26.5	35.6

The specimens in the crude oil developed black tarnish, those in neutral oil were finely pitted, and those in benzol were pitted and attacked in an intergranular manner.

Chlorinated compounds. Chlorinated hydrocarbons are in general well resisted by nickel. When hot, and in the presence of moisture, reaction rates may become moderate to high. Sastry⁴⁶ has given the following rates for substances with and without seeds. The seeds were typical oil-seeds with which these solvents were being used in extracting. The seeds were added, for test purposes, since they supplied moisture to the solvent. The substances were heated in a reflux condenser for 10 hours. See Table 251.

TABLE 251.—*Nickel vs. Chlorinated Compounds.*

Substance	Boiling Point ° F.	Mg. per sq. dm. per day	
		With Seeds	Without Seeds
Carbon tetrachloride	131	<7	<7
Dichlorethylene	190	<7	<7
Trichlorethylene	250		<7
Tetrachlorethane	300	58	250
Pentachlorethane	318	<7	220

The data in Table 252 were obtained on metal exposed to mixtures of carbon tetrachloride and water.⁴⁴

TABLE 252.—*Nickel vs. Carbon Tetrachloride.*

Conditions	Mg. per sq. dm. per day
Immersion; 6 mos., room temp.03
Vapors; 100 days, hot	127

Other tests²² in hot tetrachloride for 20 hours gave lower rates. (See Table 253.)

TABLE 253.—*Nickel vs. Carbon Tetrachloride.*

Conditions	Mg. per sq. dm. per day
Boiling liquid5
Vapor and condensate	20.6

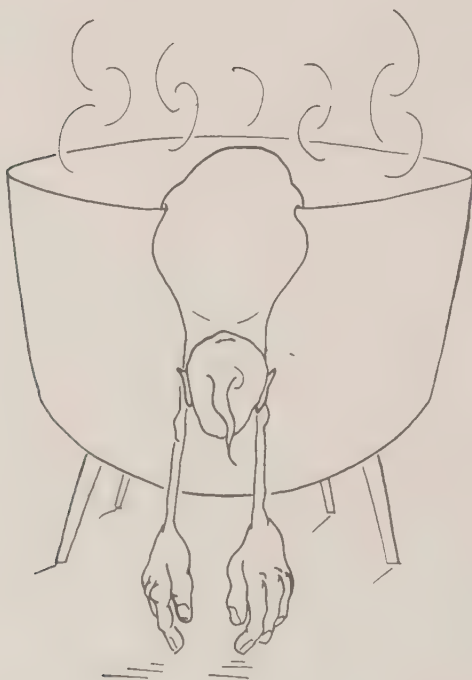
NICKEL

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Chapter XVIII

Nickel-Copper Alloys

The nickel-copper alloys are characterized by good mechanical properties, good corrosion resistance and high temperature stability, desirable appearance and versatile working properties. Their usefulness lies roughly in those engineering and equipment applications in which steels do not stand up due to corrosion and in which other non-ferrous metals and alloys, cheaper than the nickel-copper group, are deficient in either mechanical properties or corrosion resistance.

The most common of the nickel-copper compositions is the 68% nickel, 29% copper type, carrying about 3% manganese, iron, etc., as either incidental or intended additions. The first of the alloys of this group to carry wide commercial significance, Monel metal, was established in composition as the existing nickel-copper ratio in certain deposits of ore as taken from the ground. This ratio has proved to be a happy one from the standpoint of several properties. Due to availability as well as inherent characteristics, this type of alloy is widely used.

Perhaps next in importance is the composition of 40 to 45% nickel and 55 to 60% copper. Originally compounded for its high specific electrical resistance and low coefficient of electrical resistance, this group is now established to some extent in uses where its mechanical properties, corrosion resistance and appearance are useful. The 30 Ni 70 Cu and 20 Ni 80 Cu alloys, with and without 5% zinc, are used for steam condenser tubing handling salt water. Another group, essentially casting alloys, consists of about 35% nickel with small quantities of minor constituents, and the balance copper. A wrought alloy with 29% nickel, 1% tin, and the balance copper has properties typical of its nickel-copper ratio with some desirable effects from the tin. Finally, alloys with 25 to 5% nickel, balance copper, whose outstanding characteristics are ductility and low cost (as compared with the higher nickel alloys), are used for bullet envelopes and shells, coinage, etc. In strength they are inferior to the higher nickel groups.

Versatile corrosion resistance is the outstanding property and the basis for the greater part of the practical applications of nickel-copper. Among

the conditions to which they are normally resistant are non-oxidizing acid, caustic, neutral reacting solutions, food products, waters and brines, ordinary atmospheres, miscellaneous organic substances, and elevated temperatures in a range somewhat higher than that to which steel and the cheaper copper alloys are limited. Their resistance under this variety of conditions is in many cases inherently better than that of other metals.

Conditions where the use of the nickel-copper group becomes impractical, due to corrosive action, include oxidizing acid solutions, strong aqueous ammonia and powerfully oxidizing alkaline solutions, sulfidizing substances at high temperatures, and miscellaneous molten metals, fused salts, etc.

Composed as they are of copper and nickel—both with definite corrosion resistance characteristics—it is not strange that these alloys are closely similar to copper and nickel in behavior. In many cases the alloys exhibit a better resistance than either copper or nickel.

Of the various nickel-copper compositions, the Monel metal type has come to be used more than any other for purposes where chemical resistance is the chief consideration, due to availability and physical characteristics as well as to superiority in certain types of corrosion resistance. Ordinarily the differences in resistance among the alloys of the group are not marked and certainly not predictable, variations in relative behavior occurring with almost every set of corrosive conditions. For example, with a given solution a change in the degree of aeration will tend to change the order of resistance among the alloys.

TWO-METAL GALVANIC CORROSION 2, 5, 11, 82

In their two-metal galvanic relations, nickel-copper alloys in general are strongly cathodic to aluminum and the light alloys; more mildly cathodic to steel, zinc, lead, and tin, and to chromium-iron and chromium-nickel-iron in the active condition of these alloys; and anodic to passive chromium-iron and chromium-nickel-iron and to the precious metals. The galvanic relationships among metals of the copper and the nickel groups vary with different exposure conditions. Generally speaking, however, in neutral and acid aqueous conditions—where galvanic corrosion is a concern—nickel runs slightly anodic to copper, and the alloys of the two run intermediate. Nickel-copper is cathodic to the brasses.

For purposes of simplification, two-metal galvanic behavior will be considered under the headings: tap water, sea water, acid, and caustic. It is well to keep clearly in mind that the inherent corrosiveness of the solution, conductivity, and ratio of anode to cathode area are closely related to the intensity of galvanic acceleration.

Tap water is characteristically of very low conductivity and, except in the case of iron, low in inherent corrosiveness. The coupling of Monel or

other nickel-copper alloys with copper, brass, bronze or stainless steel leads to no accelerated action. Steel tends to suffer galvanic attack in couple with Monel metal, but the degree of acceleration is inappreciable practically, unless the area of the Monel metal is very large in relation to the steel. In one set of tests a small steel specimen exposed in tap water at 200° F. for 72 hours, coupled with Monel metal 150 times greater in surface area was corroded at a rate of 154 mg. per sq. dm. per day, as compared with 44 mg. when uncoupled. In this case the Monel metal was in the form of a small cylindrical tank 12 inches in diameter and 22 inches in length. The steel specimen was held inside, in from the wall. This was an unusual set-up in that the entire cathode area was within a few inches of the anode.

Soft solder often is unsatisfactory coupled with Monel metal, since the solder is definitely anodic and, used as a joint, small in area compared with the Monel metal sheet. In tests in the Monel metal tank mentioned above, at 200° F., the corrosion rate of solder jumped from 0.5 mg. per sq. dm. per day when uncoupled, to 105 mg. when coupled. Here again the cathode area was 150 times that of the anode.

Sea water, having high conductivity, offers galvanic acceleration a much better chance to take place. Steel suffers when coupled with Monel metal. A steel bolt in a Monel metal sheet goes rapidly in air-saturated sea water. When of equal areas, the corrosion rate of steel may double when coupled with Monel metal. This is true for a steel and copper couple as well.

Aluminum, zinc, lead and tin are not useful coupled with Monel metal in sea water.

The polarity in sea water of Monel metal coupled with copper, the brasses and the bronzes is not always predictable. In general the brasses and copper tend to be anodic, with the bronzes more indeterminate in behavior. In general, also, appreciable acceleration is likely only if the cathode material is present in large area. Recent tests³¹ have shown that the coupling of Monel metal with brass leads to severe dezincification of the brass. Brass coupled with Monel of four times the brass area was fairly rapidly corroded. It is more satisfactory to couple Monel metal with copper or bronze.

Stainless steel is not safely coupled with Monel metal in sea water because of the likelihood of pitting of the steel.

In *acids* the coupling of metals is more dangerous. It is almost never satisfactory to couple steel or iron with Monel metal, the exceptions being where the area of Monel metal is small—as in bolt heads—and the steel or iron section is heavy enough to handle some degree of acceleration.

Monel metal coupled with copper, copper alloys, or nickel in acid solutions tends toward galvanic acceleration. Which metal suffers is not usually predictable. The degree of galvanic acceleration runs roughly parallel to

the ratio of cathode to anode area. Generally speaking nickel will suffer in couple with Monel metal, and Monel metal will suffer in couple with copper.

Soft solder is not useful in jointing Monel metal in acid solutions. Disintegration of the solder is rapid. When the solution handled carries sulfuric acid lead joints are reasonably satisfactory because of the protective lead sulfate coating that develops. Ordinarily for acid work a silver soldered joint is the most satisfactory, this remaining cathodic or at least substantially neutral to the Monel metal.

ACIDS

The nickel-copper alloys generally speaking have good resistance to non-oxidizing acids—sulfuric, hydrochloric, phosphoric, acetic, etc.—and invariably poor resistance to acids inherently oxidizing—nitric, sulfurous, chromic, highly concentrated sulfuric. For handling the latter oxidizing group other metals are better suited. In the field of non-oxidizing acids, on the other hand, the nickel-copper alloys are among the few of widespread applicability, even though ordinarily action is sufficient to be recognizable.

Non-oxidizing acids—air-free. In the absence of air nickel-copper is not attacked, or at least very negligibly attacked, by most of these acids. For instance the action of nearly air-free 1 to 35% sulfuric is under 10 m. per sq. dm. per day. This is typical of nearly all air-free solutions of the non-oxidizing group, with the exception of hydrochloric acid of 20% concentration and higher; in this latter, attack is moderate to strong.

Non-oxidizing acids—aerated. These acids are corrosive roughly in proportion to the rate at which dissolved air reaches the surface. When the solution is quietly exposed to the air, the rate is low and consequently corrosion rates are low. Rates³¹ for a number of acids in tests where the specimens were submerged in acids held in stoppered bottles for 20 days ranged from 2 to 10 mg. per sq. dm. per day. The air available for corrosion was that present in the bottles at the beginning of the test. The acids, sulfuric, acetic, tartaric, citric, lactic, malic, tannic, varied very little one from another in corrosion rates.

Acid solutions when quiet yet freely exposed to the air are more corrosive, since these are continually replenished with dissolved air. Under these conditions rates range from 3 to 50 mg. per sq. dm. per day. The various acids are very much alike in behavior inasmuch as rates are controlled largely by rates of oxygen replenishment. Sulfuric and hydrochloric, particularly the latter, are at the higher end of this range of rates.

When the acids are agitated either by stirring or flow or with gas, so long as some part of the solution is exposed freely to the air, the rate of oxygen

replenishment is high and corrosion rates go up accordingly. The accelerating effect is particularly marked with hydrochloric—raising rates to 500 mg. per sq. dm. per day or higher—somewhat less so with sulfuric—rates of about 200—and still less with acetic and most other acids—rates of about 100. These rates apply to maximum aeration-agitation conditions. Most acid-processing solutions are intermediate between quiet and these maxima.

The effect of aeration is shown excellently by the data in Table 254⁶³ for hydrochloric and acetic against Monel metal. The solutions were one normal in strength, the temperature 86° F. and the duration 48 hours following previous exposure of 48 hours.

TABLE 254.—*Monel Metal vs. Acids.*

	Corrosion rate—Mg. per sq. dm. per day	
	Hydrochloric	Acetic
Total immersion		
Quiet	35	15
Air-agitated	520	51
Alternate immersion		
Continuous	92	23
Intermittent	25	3
Spray (30 days)	18	6

Curves given later for sulfuric and hydrochloric also illustrate the effect of aeration.

Non-oxidizing acids—effect of temperature. Increasing temperatures are almost always accelerating with this group of acids. Solutions at 200° to 212° F. are on the order of 5 to 40 times greater in attack than at room temperature.

Effect of metal composition. Against acids the various nickel-copper alloys are broadly alike in behavior. Tests in any single set of conditions, with the various factors well controlled, will bring out rather wide differences. A comparison is given in Table 255.⁶³

Hydrochloric is seen to be considerably more corrosive than acetic, particularly in the case of copper. Especially noticeable is the fact that the metals vary in resistance among themselves depending on the exposure condition. The tests bear out experience, in that Monel metal is more generally serviceable than nickel or copper in both hydrochloric and acetic acids.

Sulfuric acid.^{3, 8, 12, 17, 25, 30, 32, 47, 48, 52, 57, 58, 66, 71, 74, 78} The behavior of Monel metal in sulfuric at room temperature and at elevated temperatures⁷¹ is given in Figures 56 and 57. These and other data lead to the following conclusions:

TABLE 255.—Nickel-copper Metals vs. Acids.

Nickel %	Corrcsion rate—mg. per sq. dm. per day				
	100 Nickel	70 Monel	45 45 Ni 55 Cu	29 29 Ni 70 Cu 1 Sn	0 Copper
<i>Hydrochloric</i>					
Total immersion					
Quiet	50	35	30	55	150
Air-agitated ...	150	520	560	2800	4800
Alternate immersion					
Continuous	250	92	540	480	2790
Intermittent	85	25	40	55	550
Spray (30 days)...	20	20	40	40	20
<i>Acetic</i>					
Total immersion					
Quiet	21	15	12	18	20
Air-agitated ...	67	51	27	74	106
Alternate immersion					
Continuous	100	23	15	23	18
Intermittent	111	3	4	2	3
Spray (30 days)...	40	6	110	104	64

(1) In concentrations below 85%, sulfuric at room temperature is well resisted by Monel metal, particularly if the degree of aeration is moderate or low.

(2) Concentrations above 85% are likely to corrode Monel metal with pitting. It is better not to use Monel metal for these concentrated solutions.

(3) Monel metal is used only with caution for strongly aerated hot sulfuric.

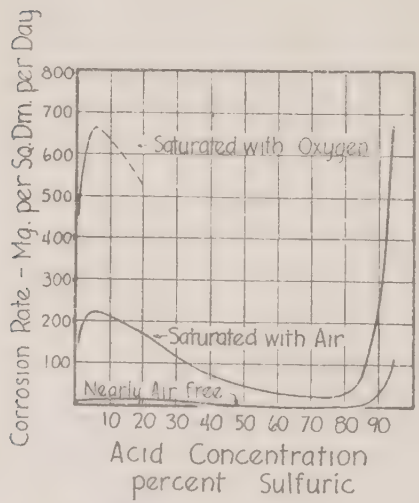


FIGURE 56. Monel Metal vs. Sulfuric Acid, Room Temperature, Agitated.

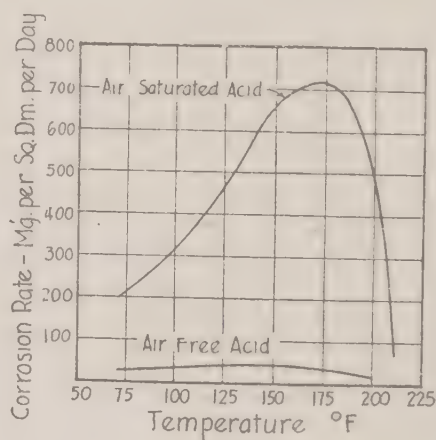


FIGURE 57. Monel Metal vs. 6% Sulfuric Acid, Agitated.

Equipment constructed of Monel metal is widely used in the pickling of steel, in which hot 5 to 10% sulfuric is the corroding solution. The oxygen content of a pickling solution becomes rather low due to the heat, the fact that the pickling reaction uses up oxygen, and the fact that hydrogen evolution tends to "wash" the bath free of dissolved oxygen. Consequently corrosion rates are low. There is the further condition that Monel metal crates, pickle pins, etc. are in galvanic couple with the steel load; the Monel metal is cathodic and therefore protected.

Hydrochloric Acid.^{3, 8, 30, 31, 32, 47, 52, 57, 63, 66, 67, 78} Hydrochloric generally is more corrosive than sulfuric acid to the nickel-copper alloys. An outline of the action on Monel metal is given in Figure 58. In quiet exposure at room temperature Monel metal may be used up to 15 or 20%. When aerated even 0.1 to 1% concentrations may be used only with caution. Solutions less concentrated than this ordinarily may be handled safely.

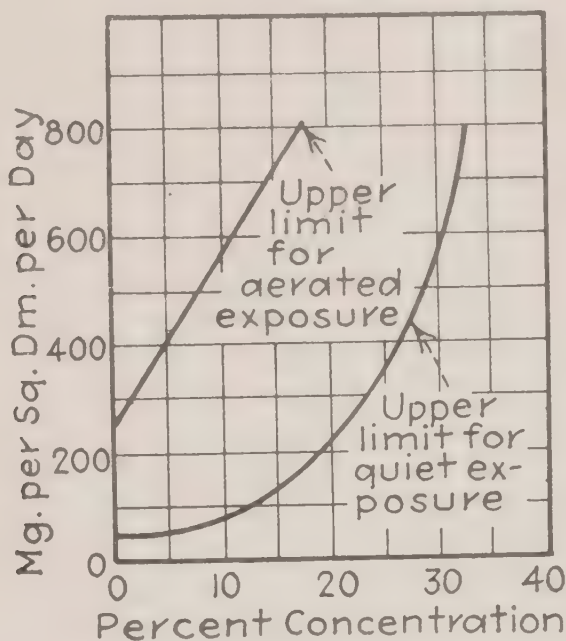


FIGURE 58. Monel Metal vs. Hydrochloric Acid at Room Temperature.

Temperature is very strongly accelerating with hydrochloric. As a rule it is better not to use Monel metal with hot acid in concentrations over 0.1 to 1% without preparing for it with heavier sections of metal.

Hydrofluoric Acid. Hydrofluoric is less corrosive than hydrochloric, and can be handled under most conditions by the nickel-copper alloys. In a 4-day test at room temperature, a quiet 48% solution corroded Monel at a

rate of 23 mg. per sq. dm. per day.³¹ At 176° F. in two hours the rate was 284 mg. per sq. dm. per day.

Nitric Acid.^{3, 8, 12, 25, 47, 66} Very dilute solutions of nitric in quiet exposure and cold corrode Monel metal at rates of 50 mg. per sq. dm. per day, and under. On the basis of these results it would seem safe to use Monel metal for concentrations of 1% or under, so long as the acid is cold, and not agitated or in flow. Yet other materials have better resistance even in this range. Acid of higher concentration or hot acid becomes very strongly corrosive. A rate as high at 1,000,000 mg. per sq. dm. per day has been observed in 70% acid.

Chromic Acid. Chromic acid, relatively weak in acid character but strong in oxidizing capacity, cannot ordinarily be handled with nickel-copper. This applies particularly to chromium-plating baths. For these other materials are more useful.

Sulfurous Acid.^{3, 36} Generally speaking, the nickel-copper alloys are not useful with sulfurous acid. The acid is oxidizing in its reaction on metal and in addition sulfidizing; the result is that a layer of metal sulfides builds up on the surface of the alloys, and under this rather severe localized corrosion is likely to take place. Solutions saturated with sulfur dioxide, aerated and agitated, give corrosion rates of 600 mg. per sq. dm. per day and greater. In moderately dilute solutions corrosion is less, but still is severe enough to make the use of the alloys inadvisable. Very dilute solutions such as atmospheric moisture carrying dissolved sulfur dioxide will produce a dark coat on the alloy but progressive corrosion is only very slow. Under these conditions of course nickel-copper is useful.

Phosphoric Acid.^{10, 32, 34, 66, 69} Phosphoric acid solutions of low aeration and at ordinary temperatures are well resisted by nickel-copper. Rates range down below 40 mg. per sq. dm. per day. Strong aeration increases

TABLE 256.—*Monel Metal vs. Phosphoric Acid.*

	Conc. %	° F.	Aeration	Mg. per sq. dm. per day
Pure acid	85.	203	No	
	25.5	203	No	22
	25.5	203	Yes	25
Pure acid				290
	50.8	176	Yes	290
	25.7	176	Yes	430
	10.3	176	Yes	860
Crude dilute		176	Yes	
(Iron—.40%)				4,300*
Crude concentr.		176	Yes	
(Iron—.73%)				610

* Pitted.

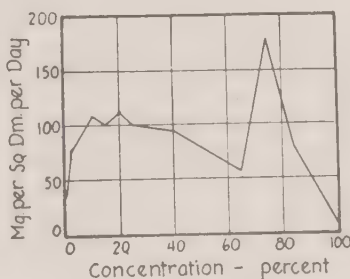
action, and elevated temperatures are relatively very accelerating. In fact these alloys may be used only with caution in hot phosphoric, rates ranging up as high as 3,000 mg. per sq. dm. per day. Sometimes hot acid is not strongly corrosive, however. (See Table 256). Crude phosphoric acid, made by interaction of sulfuric with phosphate rock, carries iron salts and consequently is likely to be very corrosive to nickel-copper.

Hot phosphoric acid solutions have given rates with Monel metal as shown in Table 256.³⁴ The duration was 24 hours or longer.

Acetic Acid.^{3, 8, 25, 30, 31, 32, 47, 52, 57, 63, 66} Acetic acid solutions can often be handled by nickel-copper. In exposure in quiet solutions at room temperature rates range around 20 mg. per sq. dm. per day. Fully aerated solutions have rates of 50 to 150 mg. per sq. dm. per day.

The data in Figure 59 define the approximate upper limit of action by acetic on Monel metal at room temperature, the tests being made in air-saturated, strongly agitated solutions. In all concentrations continuous

FIGURE 59. Air-saturated
Acetic Acid vs. Monel Metal.



films of corrosion product were formed that varied in rate of growth and physical structure with differences in acid concentration. Slight pitting took place in some cases.³¹

Elevated temperatures have the usual accelerating effect. Typical rates in boiling acid (low aeration) are given in Table 257, the duration of test being 8 hours.³¹

TABLE 257.—*Monel Metal vs. Acetic.*

Conc. %	Mg. per sq. dm. per day
10	86
26	109
56	136
90	148

On the other hand, rates in hot acid at times have been much lower. Specimens exposed to boiling acid (glacial acid with distilled water) in a reflux condenser, both submerged and in the vapor space, gave the rates in Table 258 in 20 hours.

TABLE 258.—*Monel Metal vs. Acetic Acid.*

Conc. %	Mg. per sq. dm. per day	
	Vapor	Liquid
5	8*	7.4
50	27*	13
98	9.8	11
99.9	12*	37

* Slight cement copper.

The effect of aeration is covered by the data on page 385.

Other organic acids.^{1, 14, 30, 32, 56} This group, including tartaric, malic, citric, formic, lactic, oxalic are rather similar in their corrosive effect. Quiet unaerated solutions give rates of 5 to 50 mg. per sq. dm. per day; at boiling temperatures rates increase perhaps several fold. Fully aerated solutions of these acids at room temperature range around 100 mg. per sq. dm. per day, which is within the ordinary limits of acceptable behavior.

Tests in these acids, each of 30% concentration, gave the results listed in Table 259. The tests were run for 11 days under simple immersion conditions.³¹

TABLE 259.—*Monel Metal vs. Organic Acids.*

Acid	Mg. per sq. dm. per day	
	Room Temp.	140° F.
Tartaric	7	11
Oxalic	45	50
Citric	8	42
Formic	24	142

The action of aerated acid is indicated by the data in Table 260 on 1% lactic. The solution was freely exposed to the air and at the same time constantly agitated.

TABLE 260.—*Monel Metal vs. Lactic Acid.*

° F.	Mg. per sq. dm. per day
38-50	58
145	180

Fatty acids—stearic, oleic.^{3, 47} The fatty acids are inherently much less corrosive than acids like sulfuric and acetic. Plant tests³¹ have indicated good resistance. Specimens of Monel metal exposed at the surface and below the surface, respectively, of a boiling mixture of raw grease, sulfobenzene, stearic acid, dilute sulfuric and water gave rates as follows:

Submerged	83 days.....	15.6 mg. per sq. dm. per day
Half submerged	65 days.....	15.8 mg. per sq. dm. per day

A batch was run through every 36 hours.

Even at high temperature Monel metal has good resistance to fatty acids. Exposed at 440° F. in a batch still handling a crude split stearic-oleic mixture, for three weeks, the rates were as follows:³¹

Submerged	23.6 mg. per sq. dm. per day
In vapor	15.3 mg. per sq. dm. per day

In another test³¹ in a saponifier, specimens were suspended for three months in a mixture of fatty, sulfuric, aromatic, sulfonic acids, and water, with constant agitation of live steam. Part of the time the specimens were submerged and part held at the mixture level. The rate for Monel metal was 69 mg. per sq. dm. per day.

Still further tests resulted in a corrosion rate for Monel metal of 9.3 mg. per sq. dm. per day, exposed 16 hours at 203° F. in a dry stearic-oleic mixture.³¹

Oxidizers in acid solutions. Acid solutions of the non-oxidizing type like sulfuric, sometimes carry iron, copper or other oxidizer that makes the solution more corrosive than normally. Thus acid mine waters^{49, 73} often carry as high as 0.1% sulfuric acid, 0.01% or higher ferric iron. Such a combination is too corrosive to make nickel-copper a useful handling material. A water, in constant flow with 0.2% sulfuric acid and 0.085% ferric iron, corroded Monel metal at a rate of 672 mg. per sq. dm. per day.⁷³ On the other hand acid mine waters carrying less sulfuric and iron may not be seriously corrosive. Thus with 0.04% sulfuric acid and 0.014% ferric iron the rate with Monel metal was only 86 mg. per sq. dm. per day.

Copper in acid solutions is another accelerator, if present in sufficient quantity. Thus a 6% sulfuric solution with 0.5% added copper sulfate corroded Monel metal at a rate of 2,230 mg. per sq. dm. per day. The acid was at 180° F., the duration four hours, and the solution agitated.³¹

Hydrogen peroxide is still another oxidizer. Nickel-copper in an acid solution to which peroxide is added is strongly attacked.

Sulfides in acid solutions (see also Sulfurous acid). Soluble sulfides in acid solutions react with nickel-copper to form a black metal sulfide layer on the metal. It is common for pitting to go on beneath this coating. Slight pitting had taken place on Monel metal in 6-days exposure in an agitated solution carrying suspended sulfur, at 200° F.³¹

In another test, of 6 hours duration, Monel metal was corroded at an average rate of 170 mg. per sq. dm. per day, exposed to boiling water through which hydrogen sulfide was bubbling.³²

ALKALINE SOLUTIONS

Caustic solutions.^{3, 8, 29, 47, 50, 59, 63, 72} The nickel-copper alloys are almost absolutely resistant to caustic alkaline solutions—sodium and potas-

sium hydroxides. Corrosion rates seldom rise above 6 mg. per sq. dm. per day, even at elevated temperatures; under most conditions of exposure in all concentrations of caustic the rates are considerably under this figure. Aeration in the case of caustic is not an appreciable accelerating condition.

An excellent set of data covering the action of dilute (1 normal solution) sodium hydroxide is given in Table 261.⁶³ The rates apply to a period of 48 hours following 48 hours previous exposure, and the temperature was 86° F. The spray tests were made at room temperature, and lasted 30 days.

TABLE 261.—*Nickel-copper Metals vs. Caustic Solution.*

Nickel %	Corrosion rate—Mg. per sq. dm. per day				
	100 Nickel	70 Monel	45 45 Ni 55 Cu	29 29 Ni 70 Cu 1 Sn	0 Copper
Total immersion					
Quiet3	1	.5	.2	14
Air-agitated3	1.3	.6	.3	29
Alternate immersion					
Continuous5	.4	.4	.9	14
Intermittent5	.9	.4	.5	2
Spray (30 days)3	<.1	<.1	<.1	2; <.1

Hot concentrated caustic has negligible action only on Monel metal, rates in several tests (30 to 50% solutions) ranging under 4 mg. per sq. dm. per day. As an example, specimens exposed for 380 to 384 hours in a single effect evaporator, concentrating caustic soda from 30 to 50%, at 179° F., were corroded as follows:

Monel metal	1.2 mg. per sq. dm. per day
Ambrac (20% nickel)	3.1 mg. per sq. dm. per day

Even much higher temperatures and concentrations are not corrosive. Thus, in 6-hour exposure in caustic concentrating over a temperature range of 320° to 752° F. in a vacuum evaporator, the rates in Table 262 were obtained. The caustic soda originally contained 850 grams per liter sodium hydroxide and sodium carbonate. The potash solutions originally carried 950 grams per liter potassium hydroxide.⁵⁹

TABLE 262.—*Nickel-copper Metals vs. Caustic Solutions.*

	Corrosion Rate—Mg. per sq. dm. per day	
	Caustic Soda	Caustic Potash
Monel metal	0	0.4
Copper-nickel (80/20)	0.1	0.5

Ammonia solutions.^{3, 47, 63} Aqueous ammonia involves a problem quite unlike that of caustic solutions. In dilute solutions the action is low to negligible, in concentrated solutions likely to be very strong. Ammonium hydroxide is notoriously corrosive to copper and in its higher concentra-

tions attacks nickel fairly rapidly. Yet dilute solutions are not corrosive to the nickel-copper alloys, as indicated by the rates listed in Table 263 for 1 normal solutions.⁶³ The duration was 48 hours following a previous 48-hours exposure and the temperature 86° F.; the spray test was run for 30 days at room temperature.

TABLE 263.—*Nickel-copper Metals vs. Aqueous Ammonia.*

Nickel %	Corrosion rate—Mg. per sq. dm. per day				
	100 Nickel	70 Monel	45 45 Ni 55 Cu	29 29 Ni 70 Cu 1 Sn	0 Copper
Total immersion					
Quiet	1	.5	.7	1.3	197
Air-agitated	1	.4	.3	1.7	574
Alternate immersion					
Continuous	3	1.5	1.8	9	263
Intermittent	1.8	2.6	1.5	2.5	55
Spray (30 days)	<.3	<.1	<.1	.6	42

In stronger concentrations—from about 10% up—corrosion rates for Monel metal are on the order of 50 mg. per sq. dm. per day for quiet exposure, and 1000 to 2000 mg. per sq. dm. per day for strongly aerated and agitated exposure. The presence of chlorides seems to lower the concentration at which corrosion becomes rapid.

SALT SOLUTIONS

In the case of aqueous solutions of salts,^{29, 32, 35, 47, 52, 53, 61, 62, 63} those reacting in the neutral range—e.g. sodium chloride—have negligible to no action; those reacting alkaline—e. g. sodium carbonate—have negligible to no action with the exception that alkaline hypochlorite, cyanide, and sulfide solutions are at times seriously corrosive; those reacting acid—e. g. aluminum sulfate—have mild to negligible action, with the exception that solutions of oxidizing salts like ferric and mercuric chloride have mild to strong action. Aeration is not an appreciably accelerating factor with neutral and alkaline salt solutions, yet with acid salt solutions is strongly accelerating.

Neutral salts. The rates in Table 264⁶³ give a good indication of behavior in neutral salt solutions—normal solutions of sodium chloride and potassium dichromate. The tests were made at 86° F., over a period of 48 hours following 48-hours previous exposure, with the exception that the spray test was run 30 days at room temperature. Rates of around 1 mg. per sq. dm. per day are of course practically inconsequential. These rates are typical of salts like magnesium chloride, sodium sulfate, potassium chloride, calcium chloride.

The linings of salt driers and miscellaneous other equipment handling wet salt and salt brines are often constructed of Monel metal.

TABLE 264.—*Nickel-copper Metals vs. Salt Solutions.*

Nickel %	Corrosion rate—Mg. per sq. dm. per day				
	100 Nickel	70 Monel	45 45 Ni 55 Cu	29 29 Ni 70 Cu 1 Sn	0 Copper
<i>Sodium chloride</i>					
Total immersion					
Quiet	1.2	1	1.5	2	4.5
Air-agitated	1.3	.7	5	3.6	36
Alternate immersion					
Continuous	2.2	.8	1	3.6	9
Intermittent5	1	.5	2.1	3.6
Spray (30 days).....	<.3	.4	.4	.4	2.2
<i>Potassium dichromate</i>					
Total immersion					
Quiet	2.4	.5	.5	.5	.1
Air-agitated	2	.5	.5	.3	.3
Alternate immersion					
Continuous2	2	.3	.1	.2
Intermittent4	1	.4	.1	.2
Spray (30 days).....	<.3	<.1	<.1	<.1	<.1

Acid salts—non-oxidizing. Salts reacting acid in solution are, as already stated, inclined to be more corrosive than neutral salts. Aluminum sulfate and aluminum chloride, for instance, corrode nickel-copper at rates of 20 to 30 mg. per sq. dm. per day, and even higher when the more acid solutions are strongly aerated. On the other hand rates in very dilute solutions are much lower

Acid salts—oxidizing. The soluble salts of ferric iron, acid in solution, are strongly corrosive due to oxidizing capacity. It is better not to consider using nickel-copper with solutions carrying appreciable ferric salts. Solutions of the copper salts (chlorides, sulfate, and nitrate) are acidic and oxidizing. Ordinarily these are inclined to be corrosive to nickel-copper. Silver nitrate is likewise reactive, depositing out metallic silver on these alloys. The reaction is not a rapid one, but the deposition of silver in an uneven film leads sometimes to vigorous pitting. The unsuitability of Monel metal containers for holding, in prolonged exposure (several days), photographic fixing solutions with a dissolved silver content is accountable to this set of reactions.

Mercuric salts of moderate and high concentrations attack Monel metal in an intercrystalline manner, depositing mercury out of solution, and in the case of work-strained metal tend to cause cracking. Even dilute solutions, for instance 0.1%, are not safely used in continuous contact.

Tin chloride solutions are strongly reactive with nickel-copper because of their oxidizing and acid character.

Alkaline salts. Salts reacting alkaline like sodium carbonate, sodium silicate, and trisodium phosphate can be used unconditionally with nickel-copper. An exception is hypochlorite, either calcium or sodium. Nickel

copper cannot be used in handling strong solutions of these because of rapid pitting action. Hypochlorite bleaching solutions usually carry 3 or 4 grams per liter available chlorine. Monel metal is widely used with these where the period of exposure is short (minutes rather than hours) and where an acid-souring operation or adequate flushing follows the bleach. The common hypochlorite cleaners may be used with nickel-copper without question.

Sodium and potassium cyanide are not ordinarily well resisted by nickel-copper.

WATERS

The nickel-copper alloys have good resistance to waters ^{4, 7, 18, 19, 20, 25, 37, 81} of all types—natural ground and tap waters, sea water, distilled water. Corrosion rates are negligible in exposure both to flowing and to quiet water, ranging under 1 mg. per sq. dm. per day. Aeration has no important accelerating influence. In the case of highly conductive water, as sea water, strong agitation is likely to be accelerating. Strongly agitated and aerated sea water corrodes on the order of 6 mg. per sq. dm. per day.

Tanks, conveyor lines, pump, meter, and valve parts; fittings, nozzles, etc., are common types of nickel-copper construction handling fresh and salt waters.

The nickel-copper alloys are well suited to resist sea water corrosion. Both nickel and copper are resistant and the various alloys in some ways have advantages over the pure metals. Those higher in nickel have a probably somewhat lower overall corrosion rate, while those higher in copper are more positively resistant to general pitting. The higher copper alloys are more subject to attack at the water-line, a type of attack that begins to become serious in alloys with 80% or more copper.

Nickel introduces a certain passivity in the presence of oxygen that may produce cathodic areas and stimulate local action at others. The presence of more copper lessens this tendency to localization.

Copper is fatal to a majority of the marine growths that form on most objects in the sea, particularly in harbor waters. At about 50% copper such organisms cease to grow on these alloys in many waters and at 70 Ni 30 Cu the alloys are nearly free from fouling. The absence of sea growths is desirable in itself and is further useful because pitting is reduced.

The action of sea water under two sets of conditions is indicated by ten-year tests in which East River (New York City) water passed in constant gravity flow (horizontal) through tubes. The water was recirculated, and was replenished every six months.⁴

The observations on cupro-nickels were as follows:

25 Ni 75 Cu—evenly dissolved to the extent of .002 in., but with a number of broad smooth shallow areas .020 in. deep (12 mg. per sq. dm. per day); of good appearance generally.

15 Ni 85 Cu—very smooth and evenly distributed corrosion to the extent of about .003 in., with some areas .005 in. deep (3 mg. per sq. dm. per day) ; of good appearance generally.

10 Ni 90 Cu—dissolved to the extent of .003 in. (2 mg. per sq. dm. per day), with isolated pits .020 in. deep (12 mg. per sq. dm. per day) in one tube; remaining four tubes had a fine appearance.

In one set of tests ³¹ in which specimens were submerged for 87 days in a slow tide stream of pure sea water, the results were as shown in Table 265.

TABLE 265.—*Nickel-copper Metals vs. Sea Water.*

	Mg. per sq. dm. per day
Nickel*	10-11
Monel metal*	2- 8
70 Cu 30 Ni	5-23
Copper*	22-28

*Pitted.

Condenser tubes of the nickel-copper alloys, particularly the 20% and 30% nickel compositions, with and without 5% zinc, are commonly used on turbine-driven ships, and occasionally in land power stations.^{7, 18, 19, 37, 81} The nominal velocities of the cooling water through the tubes range around 8 ft. per sec., but the water is in turbulent flow, and air bubbles carried by the water impinge against the surface of the tube. The merit in nickel-copper for these conditions—so far as the present state of knowledge would indicate—lies in the fact that the protective layers of corrosion product both resist breakdown in high degree and are self-healing. The 30% nickel alloy, in service and in laboratory tests, has given generally better behavior than the 20%.

The effect of tap water on Monel metal has been gaged by determining the drop in fatigue limit after exposure.^{21, 22, 26, 38-46} Material with an original fatigue limit of 52,000 lbs. per sq. in. had after 280 days in air-saturated water, a fatigue limit of 47,000 lbs. per sq. in. Exposed to fatigue stresses and corrosion simultaneously, the damage is more marked. Using rotating cantilever beam fatigue specimens at a rate of 1450 revolutions per minute, the fatigue strength after 100,000,000 cycles (47 days) obtained with a stream of tap water playing on the specimens, dropped to about 26,000 lbs. per sq. in. This applied as well to cold-worked metal having an original fatigue limit of 52,000 lbs. per sq. in. and annealed metal with an original limit of 36,000 lbs. Carried to 900,000,000 cycles (423 days) the fatigue strength had dropped to 10,000 lbs. per sq. in. The tests have shown also that a brackish river water is somewhat less damaging than the tap water used.

FOOD PRODUCTS

In food-processing industries, nickel-copper equipment is in common use—containers, conveyors, machine parts, table tops, etc. The suitability for this type of work ^{6, 14, 15, 23, 30, 51, 56, 70} is based, aside from structural char-

acteristics and availability, on a high degree of resistance and the practical absence of the likelihood of toxic contamination. Substances like fruit juices, milk, etc., have a free acid content, but are in general less corrosive than the corresponding pure acids of equivalent acid content. From the standpoint of life of equipment, nickel-copper is well suited for handling acid foodstuffs either at ordinary temperatures or (in most cases) at elevated temperatures including boiling.

Many processes in food preparation involve contact between the product and metal equipment of a few hours duration at the most, or in continuous processing only momentary contact before the product flows on to another step in the process. In either case, since corrosion rates for nickel-copper are low, the metal absorbed by the product is of negligible account and is not sufficient to affect the taste or change the color of the product, or to have toxic results.* It is only in cases where a given quantity of product is held in contact with metal for prolonged periods that these features require consideration.

Many foodstuffs—vegetables, meats, etc.—are practically without action on nickel-copper aside from a brown or black discoloration that develops on the metal in some foodstuffs, and that at times penetrates into the product. This is unsightly but does not signify serious attack or toxic contamination.

Fruit juices corrode nickel-copper at rates of about 5 to 10 mg. per sq. dm. per day, or less, under quiet, room-temperature exposure conditions, and at somewhat higher rates when hot.

Nickel-copper has some utility in handling milk and other dairy products. The corrosion resistance is good except under some conditions such as elevated temperatures, but prejudice against dissolved copper in milk has been strong in the dairy industry, even though the quantities absorbed from the metal equipment may be non-toxic.

A good indication of the action of milk on Monel metal is given by tests made on specimens exposed on the tubes of a surface preheater and a surface cooler respectively. Specimens on the preheater remained uncorroded whereas those on the cooler were attacked at the rates in Table 266, the temperature given applying to the milk at the point of test.

TABLE 266.—*Monel Metal vs. Milk.*

Temp. ° F.	Mg. per sq. dm. per day
43	20
64	60
79	150
144	390

Thus, milk during heating, or rather milk heated by the metal is not corrosive to Monel metal, yet when cooled by the metal is definitely corrosive.

* See chapters on Copper and on Nickel for discussions of toxicity.

ATMOSPHERE

Corrosion rates of nickel-copper in atmospheric exposure ^{9, 16, 28, 77, 80} are low, ranging down below about 3 mg. per sq. dm. per day, and usually much below this depending on factors of humidity, sulfur constituents in the air, chlorides in sea air, dirt accumulation, wash of rain, duration of exposure. The common visual evidences of change are “fogging,” tarnishing, and development of a green product. Vernon ⁷⁷ has pointed out that fogging is associated with condensation of moisture and subsequent chemical action between the moisture and the metal. Tarnishing is associated with sulfur gases in the atmosphere.

As a general rule nickel-copper in indoor atmospheres or rural (sulfur-free) outdoor atmospheres remains unchanged in appearance for relatively long periods of time. Change when it does occur takes the form of “fogging,” or loss in luster. In a sulfur-bearing urban atmosphere nickel-copper “fogs” within a few hours, and acquires a tarnish within a few days. The tarnishing develops into a brownish and greenish corrosion film. The sulfur content in the air determines the rate of this change. In applications requiring that the original luster is maintained in sulfur-bearing atmospheres, the use of nickel-copper is impractical, since the luster can be maintained only with daily cleaning.

Vernon ⁷⁷ has commented as follows: “The tendency for tarnishing is in direct proportion to the copper content, while the tendency for fogging is in direct proportion to the nickel content. Consequently, if we take specimens of copper and nickel together with a series of their alloys, and expose

TABLE 267.—*Nickel-copper Metals vs. Atmosphere.*

Atmosphere and Test Method	Corrosion Rate—Mg. per sq. dm. per day			
	Copper	20 Ni 80 Cu	70 Ni 30 Cu	Nickel
Rural				
Wt. increment098	.22	.36	.39
Resistance85	1.14	1.06	1.03
Wt. loss47	.51	.35	.28
Suburban				
Wt. increment23	.44	.83	.60
Resistance	1.5	1.35	2.12	1.68
Wt. loss71	.78	.76	.59
Mild Industrial				
Wt. increment25	.64	.96	1.40
Resistance	2.3	2.17	2.95	3.45
Wt. loss96	1.27	.83	1.35
Urban				
Wt. increment71	1.25	2.31	1.51
Resistance	1.9	2.23	4.05	3.50
Wt. loss97	1.31	1.50	1.43
Marine				
Wt. increment24	.56	.78	.87
Resistance	2.4	1.86	2.4	2.00
Wt. loss91	1.1	.70	.69

them to tarnishing conditions we find that tarnishing begins from the copper and copper-rich end of the series and falls off regularly in intensity as the copper content falls, nickel itself not being affected at all. On the other hand, if we expose them to fogging conditions, the attack proceeds from the nickel and nickel-rich end and falls off steadily to zero at the copper end." These remarks apply particularly to indoor exposure conditions, possibly to sheltered outdoor exposures.

Actual corrosion rates of nickel-copper by atmospheres are very low. The most complete set of data is that given in Table 267.²⁸ Three different criteria of damage were used—weight increment (calculated to the metal oxidized), loss in weight after cleaning, and change in electrical resistance. The duration in all cases was one year; specimens yielding the weight increment results were protected from rain, other specimens involved exposure to rain.

STEAM

The use of nickel-copper with steam^{13, 27, 33, 68} is widespread. Examples of applications are valve seats and discs, turbine blading, gaskets on steam lines, diaphragms, dehydrators. The resistance to corrosion and erosion is good. Cases of unsatisfactory behavior from wire-drawing or impingement corrosion-erosion have been traced to particularly severe conditions or to defective design.

Monel metal has been included in a number of tests covering impingement of high velocity steam. The conditions of these tests were chosen to give accelerated action:

Steam, wet for most of the time, impinged at a calculated velocity of 2900 feet per second on a Monel metal specimen held at an angle of 45°. At the end of seven weeks, with a few minor interruptions, the metal was eroded to a depth of .0007 in.³¹

A Monel metal turbine blade section after 70 hours in dry saturated steam at a velocity of 3600 to 3900 feet per second was definitely attacked in the area of impingement.²⁷

The edge of a Monel metal specimen .015 in. thick exposed 400 hours in steam flowing at 3000 feet per second became indented and the surface of sheet thinned back from the edge.³³

HIGH-TEMPERATURE ATMOSPHERES

The nickel-copper group are high temperature^{13, 24, 31, 60, 76} alloys only in the sense that they resist progressive oxidization at higher temperatures than can ordinary steels, copper, and the brasses and bronzes. There are definite limitations in their capacity to stand heat.

About 1200° F. is usually considered the upper limit of usefulness of the Monel metal type in oxidizing atmospheres. At 1200° F. the oxide film is protective; the gain in weight for the first 24-hours exposure is about 40 mg. per sq. dm. per day, and with increasing duration the rate of gain

decreases. At 1500° F. the rate of gain for the first 24 hours is about 1000 mg. per sq. dm. and this rate continues with time—in other words the oxide is not protective. Thus, between 1200° and 1500° F. a change takes place in the physical characteristics of the oxide such that it no longer is effectively protective and deterioration is rapid.³¹

The oxidation characteristics of nickel-copper in an atmosphere of oxygen in a range of 1382° to 2012° F. have been studied by Pilling and Bedworth.⁶⁰ They found that the curve of oxidation against time at a given temperature is a simple quadratic parabola, the square (3/2 power for the intermediate nickel-copper range) of the amount of oxidation being proportional to the time of exposure.

In Figure 60 are reproduced the results of Pilling and Bedworth. Wire specimens were held one hour in an oxygen atmosphere at 760 mm.

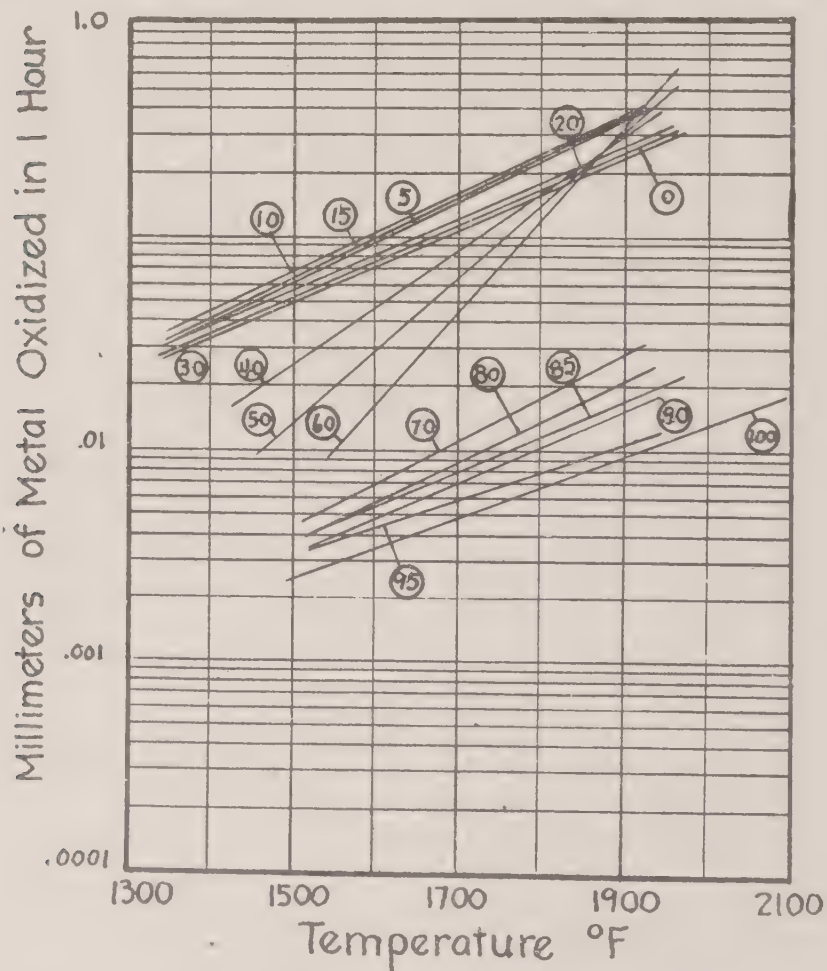


FIGURE 60. Oxidation Rates of Nickel-Copper Alloys. Nickel Content Indicated.

pressure. The unit of attack is mm. of metal oxidized as calculated from the weight increase when using an oxide metal ratio found experimentally to be a sound basis.

Sulfur gases in a hot reducing atmosphere are highly damaging to nickel-copper, at temperatures of about 700° F. and higher. At lower temperatures a surface blackening takes place, which develops into a heavier scale that is protective. At temperatures even below 700° F. the action is somewhat damaging. For instance, after 7 days in a one to ten mixture of hydrogen sulfide and natural gas at 625° F. a Monel metal specimen after removal of the sulfide scale had lost .001 to .002 in. on the exposed surface. On the other hand after 24 hours in a one to ten mixture of sulfur dioxide and natural gas at the same temperature Monel metal had suffered no more than a slight surface blackening. Monel metal used in hydrogen sulfide gas running at times up to 1000° F. failed after six weeks by severe intergranular embrittlement.³¹

An oxidizing atmosphere carrying sulfur tends to form a less protective scale than gas without sulfur. Pure sulfur dioxide at 1292° F. has been found to be about twenty times more damaging to Monel metal than pure oxygen. Very low contents of sulfur dioxide in air at temperatures under about 1200° F. would not be expected to be damaging.

In the heating of nickel-copper for forging (1850° to 2150° F.) or in annealing (1200° to 1900° F.) it is extremely important to avoid gases carrying sulfur. Even very small contents of sulfur will result in embrittled surface even though the period of exposure is short.

Monel metal is not useful in handling hot reducing ammonia gases. Vanick⁷⁶ found that a Monel metal tube of .35 in. wall had suffered intergranular fissuring after 28-hours exposure at 932° F. The metal was under 1500 lbs. internal pressure, and the gas consisted of 8% ammonia in a three to one hydrogen to nitrogen mixture. At 1274° F. a Monel metal rod, under no stress, had swollen to a loose-fibered incoherent mass after four months. Monel metal has reasonably good resistance in nitriding gas mixtures up to about 1085° F. Above this deterioration is rapid.

MISCELLANEOUS

Molten metals. Nickel-copper is not commercially suitable for handling molten metals, with the exception of mercury. Tin, aluminum, lead, zinc are more or less rapid in their attack. Tin and nickel form an eutectic alloy which melts at 425° F. The melting point of tin is 450° F. Aluminum forms alloys with copper and nickel at temperatures of 1013° and 1166° F. respectively. Aluminum melts at 1214° F. Lead alloys with nickel at the melting point of the former, 620° F.; it forms no definite alloys

with copper. A eutectic of zinc and nickel melts at 786° F., which is the melting point of zinc.

Monel metal (doubtless other nickel-copper alloys likewise) is well adapted for use with mercury. It is necessary, however, to avoid using strain-hardened metal, since even at ordinary temperatures this at times has suffered intercrystalline cracking. When properly annealed, cracking will not take place at ordinary as well as elevated temperatures. Exposed 15 days at 720° to 760° F. annealed Monel metal mercury bulbs became amalgamated at a few scattered patches. In other tests of 17 days at the same temperatures the surface of Monel metal became coated with amalgam.

Sulfidizing substances. Nickel-copper, as already stated, is sensitive to sulfidization. Fused sulfur (248° F.) for instance attacks it strongly and organic sulfur-bearing compounds of various kinds ⁷⁹ react to the extent at least of a tarnish or sulfide coating. Where the substance is acid, pitting sometimes takes place beneath this coating. As an example, specimens of Monel metal exposed 55 days both submerged and in the vapors above large volumes of crude light oil, neutral light oil, and motor benzol were pitted lightly to severely with the exception of those submerged in crude light oil. The specimens in the motor benzol exposure were corroded at average rates of 55 mg. per sq. dm. per day, with severe pitting.³¹

Chlorinated hydrocarbons. Nickel-copper is generally suitable for handling the chlorinated hydrocarbons. In clean carbon tetrachloride at room temperature, with and without moisture, rates of Monel metal range under 2 mg. per sq. dm. per day. Specimens exposed in a dry-cleaning carbon tetrachloride still were corroded at rates of 5 mg. per sq. dm. per day and less, whether in the liquid or in the vapor phase. Other tests have shown that in the hot substance, corrosion of Monel metal is less if water is absent than if present, and is less in the presence of air than in the absence of air. In a 100-hour test a rate of 94 mg. per sq. dm. per day was obtained in exposure in the vapors from a boiling mixture of tetrachloride and water.⁶⁵ Under the conditions of the test practically all air seems to have been excluded. This contrasts with the rate (maximum) of 5 mg. per sq. dm. per day, mentioned above obtained in stills in the presence of air.

Chloroform, ethylene dichloride, and trichlorethylene are likewise well resisted by nickel-copper.

Iodine. Iodine vapors and tincture of iodine attack nickel-copper strongly.

Alcohol, acetone. These substances, with and without water, are not corrosive to nickel-copper. Monel metal exposed 6 hours in a mixture of 70% ethyl alcohol in water at 104° F. was corroded at a rate of 1.2 mg. per sq. dm. per day.³¹ Monel metal exposed 6 months at room temperature

in acetone and methanol respectively, and 30 days in the vapor from the boiling substances, showed no weight loss.⁶⁴

NICKEL-COPPER

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Chapter XIX

Copper

Copper combines high corrosion resistance in atmospheres, waters and chemicals with high electrical conductivity. This combination is supplemented by several other characteristics of significance, both general and limited. High heat conductivity, workability and availability need especial mention. The resistance of copper in atmospheric exposure is particularly felicitous, for it means that no protective coatings are necessary (in contrast to iron) on the tremendous amount of copper exposed outdoors and indoors for electrical and other purposes. It is very widely used in handling acid and salt solutions and waters.

The great ductility of copper is of advantage in processes of fabrication. Where greater strength than that of copper is desirable innumerable alloys high in copper are available. These are treated in another chapter.

Commercial wrought copper is of relatively high purity—greater than 99.90% copper. "Tough pitch" copper carries a low intentional content of oxygen; in deoxidized copper the oxygen content is reduced virtually to zero. Whereas the oxygen-bearing copper is a particularly sound and strong variety, deoxidized copper is advantageous in resisting hot reducing gases in service or in hot working operations. In England, small additions of arsenic are considered useful for improving strength, and also atmospheric corrosion resistance.

Copper has wide general commercial corrosion resistance. It holds a cathodic or noble position in relation to oxidation by hydrogen ions, which gives it good resistance against acid solutions of low oxidizing capacity. Its resistance to the atmosphere and to waters is of the greatest significance. Exceptions to substances in which copper has general wide corrosion resistance are oxidizing acids, aqueous ammonia, and some strongly corrosive substances such as iodine and chlorine. Copper has extensive use in handling food products. It is limited for conditions in the high temperature range by both its low strength and relatively unprotective oxides.

The reluctance of copper to corrode due to its inherent cathodic (noble) nature is obscured in a few cases by special factors that are accelerating. Thus, it is relatively sensitive to metal-ion solution cell action, and it forms

soluble double salts in certain ammonia and cyanide solutions. Again, the presence of oxidizing agents seriously reduces its natural resistance to acid solutions.

SOLUBILITY OF COPPER COMPOUNDS

The dependence of corrosion resistance on solubilities of corrosion products is usually an obscure one, and is particularly so in the case of copper. Two examples of such dependence are the development of insoluble basic salts—sulfate and carbonate—in atmospheric exposure, and of cuprous oxide in fresh waters,³² in smoky atmospheres and at high temperatures.¹⁵ These valuably increase the naturally high resistance. On the other hand, high solubility of complex cupric ammonium compounds in aqueous ammonia, and the solubility of the cyanides of copper in potassium cyanide, help account for the strong corrosion of ammonia and cyanide solutions.

TWO-METAL GALVANIC CORROSION

Copper is one of the more cathodic metals; in fact, generally, only passivated chromium metals are more cathodic.

In exposure to the milder types of neutral reagents, such as fresh water, rain water, very dilute salt solutions and moist atmosphere, the galvanic attack that may result when copper is coupled with the copper alloys, nickel, lead, and tin is negligible to non-existent. With iron¹⁸ there is a tendency towards greater attack than with these other metals, the action of course being concentrated on the iron. These corrosives are poor electrolytes as a rule and for that reason suppress the galvanic currents. Nevertheless, the coupling of aluminum with copper in them is often unsafe practice, in view of the unusual sensitiveness of aluminum to coupled corrosion. Yet in the case of aluminum, coupling with copper (high copper alloys) in ornamental metal work in outdoor urban atmosphere, has not usually led to undesirably great attack.

As neutral solutions become more concentrated in salts, and therefore better electrolytes, the danger in using copper couples becomes more pronounced.¹⁸ This applies to solutions of the various neutral salts. Aluminum should not be coupled under these conditions, and relatively large surfaces of copper coupled with iron are likely to prove unsatisfactory. Lead, tin and solder may at times suffer attack. The high copper alloys and the nickel alloys on the other hand, since these have but very slight tendency to corrode uncoupled in such solutions, can be safely used in this group of corrosives.

The situation in neutral chloride solutions, such as brines and sea water, is quite unlike that in the other neutral salt solutions. The possibility of danger in copper coupled with iron, lead, tin becomes more pronounced;

and the brasses in couple with copper may suffer an undesirable degree of accelerated corrosion. Large surfaces of copper, such as sheathing on boats or tank linings, are likely to have an appreciable effect on brass fittings or pipes, for instance, that may be in circuit with the copper. The copper alloys low in zinc or free from zinc are less inclined to be attacked coupled with copper.

An example of a possible high degree of acceleration of iron corrosion when coupled with copper, is the case of a fully aerated, agitated, moderately dilute sodium chloride solution. In this, uncoupled iron corroded at a rate of 350 mg. per sq. dm. per day, whereas when coupled with a copper specimen of about twenty times its area, the rate was 7,900 mg. per sq. dm. per day—an increase of about twenty times.⁴⁴

As will be noted later on, copper is particularly reactive with chloride salts as compared with other neutral salts. In line with this is the result of some galvanic tests made in aerated sea water, in which Monel metal, normally slightly anodic to copper, behaved cathodically, with a rapid increase in the attack of the copper.⁴⁴

In acid exposure it is well where possible to avoid coupling copper with other metals, particularly with iron. In many cases of course it is not possible to avoid this. Perhaps the least danger in such exposure would result from copper coupled with the high copper bronzes. In fact the cast bronzes carrying tin, lead and zinc (low) are often used with copper equipment handling acids. Monel metal likewise approaches copper in electrochemical nature and often in acid exposure may be coupled with copper. On the other hand brasses of relatively high zinc content are likely to suffer severely.

ACIDS

Copper is widely employed in apparatus handling acid solutions in chemical plants.

A fairly definite division line exists between those acids that can be used at times with copper and those that cannot. The inherently non-oxidizing acids such as acetic, sulfuric, hydrochloric, phosphoric are generally well resisted by copper so long as the content of dissolved oxygen, or of oxidizing impurities such as ferric salts, is fairly low. There are exceptions to these generalizations, such, for instance, as the fact that concentrated hydrochloric acid will corrode copper rapidly, independently of the presence of oxidizing substances.

It is a difficult matter to express the oxidizing capacity of a solution when this oxidizing capacity is derived from a content of dissolved oxygen (air). As a rule a thoroughly agitated or stirred solution, or one into which an air-stream is directed, approaches air-saturation. A solution of an acid that is in itself non-oxidizing, under aerated conditions becomes very

definitely corrosive to copper. This generalization applies both to strongly ionizing acids like sulfuric, hydrochloric, and formic, and to weakly ionizing acids like acetic. Although the acid concentration and to a lesser extent the hydrogen-ion concentration, are factors in determining corrosion rates—the rates in general tending to increase with each of these factors—the importance of these factors is overshadowed by the variable of dissolved oxygen content (aeration) within the limits that this variable exists in the actual use of metals. Acids of inherent oxidizing capacity, such as nitric, sulfurous, and concentrated sulfuric, and acids carrying oxidizing impurities such as ferric salts, cannot be handled in copper equipment—at least these are more economically handled by other metals and alloys. Sulfurous acid, while generally considered reducing, acts as an oxidizing acid in the corrosion of metals, furnishing oxygen and sulfur for combination and accelerating the corrosion as much as or more than the true oxidizing agents.

The action of acids on copper may be generalized as follows:

1. In very dilute acid solutions, ranging from neutral to concentrations on the order of .01 per cent, the action on copper is relatively low, the rates ranging well below 60 mg. per sq. dm. per day. This is true of oxidizing acids like nitric as well as of non-oxidizing acids like sulfuric, and the action is relatively insensitive to the accelerating effect of aeration.
2. Non-oxidizing acids with an air content approaching zero have practically no corrosive effect, independent of concentration; thus rates in 1.2 normal sulfuric, hydrochloric, and acetic acids in the absence of air were less than 1 mg. per sq. dm. per day.⁶² Air free solutions are rarely met, but the fact that copper is virtually uncorroded by them is significant.
3. Solutions of non-oxidizing acids (hydrochloric excepted) carrying air in such quantity as is absorbed in quiet contact with atmosphere are rather weakly corrosive, independently of concentration. The rates are roughly 5-60 mg. per sq. dm. per day.
4. Air-saturated solutions of non-oxidizing acids are likely to be rather strongly corrosive,—on the order of 50-300 mg. per sq. dm. per day, and higher for hydrochloric acid. The actual corrosion rate in any individual case will depend in some degree on hydrogen ion concentration and certain other factors difficult to classify.
5. Oxidizing acids except in very dilute solutions corrode copper rapidly—roughly above 500 mg. per sq. dm. per day—independently of aeration. This is true of both inherently oxidizing acids—nitric—and acids whose oxidizing capacity is due to impurities such as ferric iron.

To define more specifically the bounds within which these generalizations apply, it is necessary to say that at temperatures above ordinary room temperatures the rates are higher; that with very low concentration acid solutions—indefinitely below 0.01 per cent—the effect of aeration becomes relatively low; that the solubility of oxygen in acids, varying as it does with the acid concentration, is a further variable in determining corrosion rates; and that the development of low solubility corrosion products often is directly suppressive.

The rates in Table 268³⁵ are particularly instructive in that three types of corrosion reaction are expressed. The high rate for nitric reflects a powerful acid-oxidizing combination. In the case of hydrochloric the corrosion was accompanied by hydrogen evolution, and was independent for the most part of dissolved oxygen. Finally, sulfuric corroded only so fast as oxygen was supplied by diffusion through the solution. The test conditions were simple immersion, for 24 hours at 59°F.

TABLE 268.—Copper vs. Acids.

Acid	Mg. per sq. dm. per day
Nitric—32%	57,000
Hydrochloric—conc.	180
Sulfuric—17%	20

Under the same conditions the action of phosphoric, acetic, tartaric, formic, oxalic, malic, etc., would be more like that of sulfuric.

Aeration. The effect of a number of acids of 1% concentration under quiet partial immersion conditions in sealed containers is indicated by the data in Table 269. The tests were made at 70° F. with five days duration.⁴²

TABLE 269.—Copper vs. Acids.

Acid—1%	Mg. per sq. dm. per day
Hydrochloric	142
Sulfuric	28
Acetic	27
Butyric	17
Lactic	15
Citric (0.2%)	14

The aeration factor is well shown by the data in Table 270.⁶² Gas was bubbled through the solution for one hour previous to exposure of the specimens, the ratio of nitrogen and oxygen in the gas being varied. The temperature was 72° F. and the duration 24 hours.

TABLE 270.—Copper vs. Acids.

Oxygen in Gas Per Cent	Corrosion Rate—Mg. per sq. dm. per day		
	Sulfuric 1.2 N	Hydrochloric 1.2 N	Acetic 1.2 N
0	<1	<1	<1
5.5		69	
10.4	23	210	21
15		260	
16.1	36		39
21 (air)	58		39
24.5			59
26.4		540	
27.4	65		

Aeration is further covered by the data in Table 271,⁷⁷ from tests in which hydrogen and oxygen gas respectively were bubbled through the

solution. Rates with oxygen gas are higher than would be obtained with air as the gas. The tests were made at room temperature, with five-hours duration.

TABLE 271.—*Copper vs. Acids.*

Acid	Corrosion Rate—Mg. per sq. dm. per day	
	Oxygen	Hydrogen
Sulfuric		
6%	920	22
20%	840	36
96.5%	250	35
Hydrochloric		
4%	8,600	105
20%	13,400	75
Acetic		
6%	143	8
50%	445	19
Glacial	12	12
Citric		
50%	170	29

Different exposure conditions involving various degrees of aeration are covered by the data ²⁷ in Table 272. These are particularly useful in that a strong corrosive—hydrochloric—and a relatively weak acid—acetic—are compared. The tests were made at room temperature, for a 48-hour period following previous 48-hour exposure. The spray tests ran 30 days.

TABLE 272.—*Copper vs. Acids.*

Exposure	Mg. per sq. dm. per day	
	Hydrochloric 1 N	Acetic 1 N
Total immersion		
Quiet	320	18
Air-agitated	5,000	65
Alternate immersion		
Continuous	3,200	35
Intermittent	800	14
Spray (30 days)	290	76

Temperature. The accelerating effect of temperature rise is different in intensity for the different acids, and also for different aeration conditions. Data are very meager, but the two sets in Tables 273 and 274 suggest the order of acceleration.

Tests have been made ⁴² in 1% acid solutions, with specimens partially immersed in the liquid held in sealed containers. The duration at room temperature was 5 days, for the warm tests 5 hours.

TABLE 273.—*Copper vs. Acids.*

Acid	Mg. per sq. dm. per day	
	70° F.	145° F.
Lactic—1%	15	73
Butyric—1%	17	109

In the following tests the specimens were simply immersed, without artificial aeration of the acids:⁴⁵

TABLE 274.—*Copper vs. Acids.*

Acid	Hours Room temp.	Mg. per sq. dm. per day	Hours 194–212° F.	Mg. per sq. dm. per day
Sulfuric				
5	7	77	7	120
10	7	51	7	150
20	7	26	7	110
Citric				
Sat'd.	24	3	2	56
Lactic				
25	24	20	2	403
Phosphoric				
85	24	6	2	35

Oxidizers. Oxidizers in solutions of the non-oxidizing acids are very strongly corrosive. The principal oxidizers encountered are ferric, cupric, stannic, mercuric salts. A number of illustrations are given in Table 275. In one set of tests⁶⁸ specimens were exposed to running mine waters carrying sulfuric and ferric sulfate, at ordinary temperature.

TABLE 275.—*Copper vs. Oxidizing Acid Solutions.*

Water	Days	Mg. per sq. dm. per day
Sulfuric — .14%		
Ferric iron .006%	119	189
Sulfuric — .22%		
Ferric iron .09%	33	706
Sulfuric — .04%		
Ferric iron .01%	98	130

Other oxidizers were added to acids, with the results in Table 276.⁷⁶ The tests ran for 19 to 22 hours at 100° F.

TABLE 276.—*Copper vs. Acids.*

Acid	Mg. per sq. dm. per day
Hydrochloric—1 N	230
Hydrochloric—1 N	
Potassium permanganate—5%	9,000
Sulfuric—1 N	43
Sulfuric—1 N	
Potassium dichromate—5%	5,600
Sulfuric—1 N	
Sodium chlorate—5%	8,500

Nitric acid.^{33, 35, 43, 50, 70} Nitric acid, except in extremely dilute solutions, should not be considered suitable for contact with copper. In simple quiet submersion, in .06% acid, a rate of 20 mg. per sq. dm. per day has

been reported.⁴³ Perhaps 0.1% acid should be taken as the upper limit for satisfactory performance. In moderate concentrations rates run up to over 1000 mg. per sq. dm. per day, and in concentrated acid far above this.

Sulfurous acid. Sulfurous acid solutions are strongly corrosive to copper, more by pitting action than by weight loss. Copper is usually satisfactorily resistant to smoky industrial atmospheres, but in some cases, as in flue linings exposed to moist sulfurous gases in high concentration copper is badly attacked.

Phosphoric acid.^{45, 47, 59, 63} Tests on copper have been made,^{59, 63} by quiet submersion for 250 hours at 60° F. in acid obtained by combustion of phosphorus and by leaching of superphosphate, respectively. The latter was far more corrosive due to the presence of ferric iron as an impurity. (See Table 277.)

TABLE 277.—*Copper vs. Phosphoric Acid.*

	Mg. per sq. dm. per day
Pure phosphoric	
76%	50
42%	100
Impure phosphoric	
42%	300

Aeration of phosphoric has the normal accelerating action; heat is abnormally accelerating with phosphoric. A number of tests in hot acid, pure and impure (ferric iron) gave the results shown in Table 278.

TABLE 278.—*Copper vs. Phosphoric Acid.*

	Mg. per sq. dm. per day
Pure acid	
85%, unaerated, 203° F.	29
25%, unaerated, 203° F.	105
25%, aerated, 203° F.	2,200
50%, unaerated, 176° F.	220
25%, unaerated, 176° F.	410
10%, unaerated, 176° F.	490
Impure, crude acid	
Dilute, unaerated, 176° F.	4,500
Concentrated, unaerated, 176° F.	2,100

Hydrochloric acid.^{9, 22, 27, 33, 35, 42, 43, 50, 51, 62, 70, 76, 77} Hydrochloric acid is so corrosive to copper that concentrations higher than about 0.1% cannot for most purposes be handled with it. In .03% acid under quiet submersion conditions rates of 25 mg. per sq. dm. per day have been reported.⁴³ At 0.1% the rates in simple immersion exposure are around 100 to 200 mg. per sq. dm. per day, and rapidly increase with higher concentrations, temperatures, and particularly with aeration. In concentrations above about 30% at room temperature and 20% in the higher tem-

perature range (e. g. 167° F.), the corrosion reaction goes on with strong hydrogen evolution, as indicated in Figures 61 and 62.²²

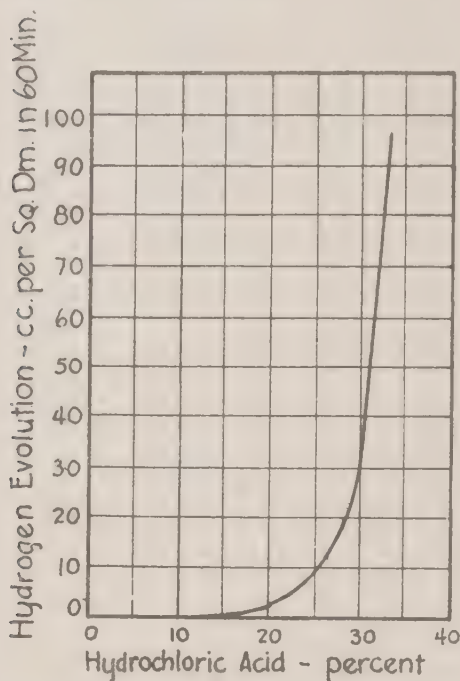


FIGURE 61. Copper vs. Hydrochloric Acid at 167° F.

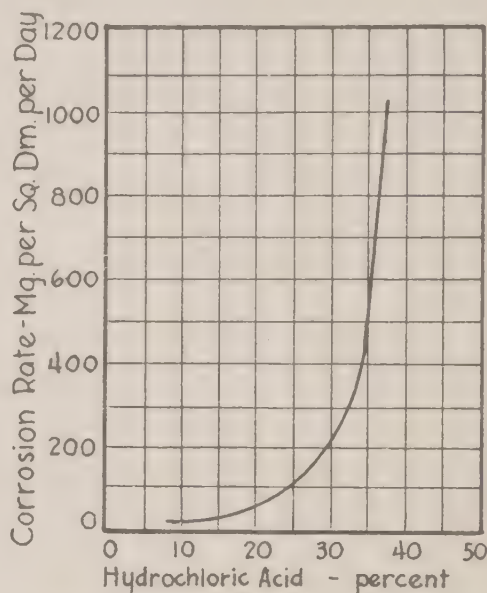


FIGURE 62. Copper vs. Hydrochloric Acid at 68° F.

Sulfuric acid.^{13, 33, 35, 42, 43, 44, 50, 51, 62, 76, 77} As a summary of the evidence on the sulfuric acid attack of copper, the following seem to be true as generalizations:

1. Concentrations higher than about 80% in the cold and about 60% hot are too corrosive to warrant the use of copper. In concentrated acid, the corrosion reaction does not require, though is aided by, the presence of dissolved oxygen, and progresses with the partial breakdown of the acid into reduced sulfur and free oxygen, both of which tend towards further corrosion. The action takes the form characteristically of pitting beneath a sulfide scale.
2. Concentrations below 80% that are free of dissolved oxygen do not corrode copper at all at room temperature and but slightly at elevated temperatures.
3. Concentrations below 80% with low content of dissolved oxygen (unagitated solutions exposed to the atmosphere) corrode copper at rates of about 20 to 80 mg. per sq. dm. per day. The actual acid concentration is a minor variable, a range from .01 to 80% yielding corrosion rates of the same order. At elevated temperatures the rates are perhaps 50 to 120 mg. per sq. dm. per day.
4. Concentrations below 80% under fully aerated conditions (strong agitation) corrode at rates of about 150 to 300 mg. per sq. dm. per day. The conditions at the solution-air-metal contact of a quiet solution approaches full aeration. At elevated temperatures (below about 60% concentration) the rates are 100 to 400 mg. per sq. dm. per day. Concentrations within the range of 1 to 20% are the most corrosive, hot or cold.

Quiet submersion in .05% sulfuric at room temperature for a 7-day period gave a rate of 17 mg. per sq. dm. per day,⁴³ indicating the action of very low concentrations.

Temperature, concentration and aeration as variables were involved in Table 279.⁷⁷ The tests were of 5 hours duration. Hydrogen and oxygen respectively were bubbled through the solution.

TABLE 279.—*Copper vs. Sulfuric Acid.*

Sulfuric Acid Conc. %	Temp. ° F.	Mg. per sq. dm. per day	
		Oxygen	Hydrogen
6	68	920	21
20	68	840	36
96.5	68	250	35
6	95	2,300	54
20	95	1,300	51
96.5	95	300	62
6	122	2,700	75
20	122	600	62
96.5	122	520	260

These rates for oxygen-saturated acid are much higher than would apply for air-saturated acid. The rate in air-saturated 6% acid at room temperature would be about 200 to 250 mg. per sq. dm. per day.⁴⁴ Although the rate given above in room temperature, concentrated acid under hydrogen is low, copper is ordinarily not recommended for concentrated sulfuric.

Hot 6% acid, aerated and unaerated, gave the rates in Table 280.⁴⁴

TABLE 280.—*Copper vs. Sulfuric Acid.*

Temp. ° F.	Mg. per sq. dm. per day	
	Unaerated	Aerated
140	105	280
160	95	330
178	145	370
194	153	410

Acetic acid.^{9, 16, 27, 42, 44, 51, 53, 62, 77} Copper equipment is used a great deal in commercial processes involving exposure to acetic acid, e. g., in the process of manufacturing acetic acid from calcium acetate and sulfuric acid. Although available corrosion rates indicate that the action of hot mixtures of acid and acetic anhydride, and hot glacial acid may sometimes be severely corrosive, ordinarily the rates of acetic, dilute or concentrated, boiling or cold, aerated or unaerated, fall below 300 mg. per sq. dm. per day. There is a tendency towards pitting, but its details are not clearly enough known to be stated.

To generalize, the action of acetic is somewhat as follows:

Cold, unaerated solutions, up to 100% concentration—under 50 mg. per sq. dm. per day.

Cold, aerated solutions, up to 100% concentration—50 to 200 mg. per sq. dm. per day.

Hot solutions, unaerated or aerated, in concentrations to 100%—20 to 1000 mg. per sq. dm. per day.

Mixture of anhydride and acid—in the cold up to 300, in the hot up to 3000 mg. per sq. dm. per day, with the degree of aeration of slight and variable significance.

Tests have been made⁴⁴ in boiling mixtures of glacial acetic and distilled water, of 20-hour duration. (See Table 281.) „

TABLE 281.—*Copper vs. Acetic Acid.*

Acetic Acid Conc. %	Mg. per sq. dm. per day	
	Vapor Phase	Liquid Phase
5	19	22
50	72	46
98	67	176
99.9	15	137

Hydroxy-acids.^{9, 16, 42, 53, 77} The hydroxy-acids as a whole behave not unlike acetic, so far as the limited data are an indication. In unaerated solutions at room temperatures, the rates for formic, butyric, lactic, citric, tartaric, malic are on the order of 6 to 70 mg. per sq. dm. per day. Aeration is accelerating to the extent perhaps of three or four-fold. At temperatures up to boiling the rates range up to 120 mg. per sq. dm. per day, sometimes up to 300. Differences in corrosiveness among the acids exist but they are of minor degree and their nature impossible to classify.

Chloroacetic acid is known to be very corrosive. A boiling solution (spec. grav. 1.36) has given a rate of 1400 mg. per sq. dm. per day.⁹

Fatty acids. The fatty acids attack copper, producing green copper soaps.* Rates of 25 mg. per sq. dm. per day were obtained for copper exposed, submerged and in the vapor phase respectively, within a still handling crude split oleic and stearic acids at 440° F. under vacuum.⁴⁴ Three months in a saponifier handling a boiling solution of 60% fatty acids and small contents of sulfuric, aromatic, and sulfonic acids led to a rate of 100 mg. per sq. dm. per day.⁴⁴

Hydrogen sulfide. In aqueous solution, particularly in the presence of other acids, hydrogen sulfide rapidly blackens and corrodes copper.

ALKALINE SOLUTIONS

Caustic. Copper is only slowly corroded by caustic alkalies, but the action is appreciable. Since iron is less affected and costs less, copper is rather rarely an economical material of construction for handling alkalies. Where copper is desirable for other reasons it may resist some alkaline solutions, not ammonia, in a satisfactory manner. Rates in Table 282 were obtained in tests at 86° F. which ran 48 hours following 48 hours previous exposure.²⁷

* W. H. Bassett, private communication.

TABLE 282.—*Copper vs. Sodium Hydroxide.*

Condition	Mg. per sq. dm. per day
Total immersion	
Quiet	14
Air-agitated	20
Alternate immersion	
Continuous	29
Intermittent	14
Spray	2

Lower rates have been reported in some tests^{33, 41, 43} and higher rates for caustic soda and potash in others.^{13, 41, 50}

Hot caustic soda, concentrating from 30 to 50% at 179° F. has given a rate of 14 mg. per sq. dm. per day.⁴⁴ Still further tests, in concentrated caustic potash and caustic soda in a vacuum evaporator over a temperature range of 320 to 752° F. gave rates below 1 mg. per sq. dm. per day.⁵⁶ Again a mixture of 10 parts caustic potash and 7 parts caustic soda, concentrating from 25° to 50° Bé yielded a rate of 120 mg. per sq. dm. per day.⁹

Fused caustic at 660° to 1100° F. has been reported⁷⁵ to be very corrosive to copper, yet with the addition of 5% sodium peroxide to the fusion, the action, at least in the 660° to 750° F. range, was greatly suppressed.

Aqueous Ammonia.^{13, 50} Ammonium hydroxide is one of the most rapidly reactive substances with copper, due to the formation of highly soluble copper-ammonium compounds. Advantage is taken of the solubility of copper compounds in ammonia in the use of ammonia polishing mixtures for removing the tarnish films from copper.

Very dilute solutions of ammonia may be fairly low in their action. For instance, exposure in .01 normal ammonium hydroxide in quiet immersion at room temperature for a week led to a rate of 15 mg. per sq. dm. per day.⁴³

The action of intermediate concentrations is well outlined by Table 283.²⁷ The solution was 1 normal strength, and the test period 48 hours following a previous 48-hour exposure; the spray test was run for 30 days. All tests were at room temperature.

TABLE 283.—*Copper vs. Ammonium Hydroxide.*

Condition	Mg. per sq. dm. per day
Total immersion	
Quiet	160
Air-agitated	430
Alternate immersion	
Continuous	870
Intermittent	205
Spray (30 days)	35

Aeration is strongly accelerating.

The extremely rapid attack under strong aeration and agitation is indicated by Table 284.⁴⁴ The tests ran 3 to 7 hours at room temperature.

TABLE 284.—*Copper vs. Ammonium Hydroxide.*

Ammonia %	Mg. per sq. dm. per day
26.7	19,000
10.6	27,000
6.5	41,000
4.2	66,000
2.4	53,000
1.0	38,000

SALT SOLUTIONS

Copper has excellent resistance to many salt solutions, such as the sulfates and nitrates of sodium and potassium, reasonably good resistance to others like the chlorides of sodium and calcium, which is of the greatest economic value in marine uses, and poor resistance to oxidizing substances like ferric and cupric salts, and to ammonia salts. Rates range from less than 1 mg. per sq. dm. per day in the first group, to 4 to 70 mg. per sq. dm. per day in the non-oxidizing chlorides, and greater than this in the oxidizing-acid and the ammonia salts.

The data in Table 285²⁷ compare sodium chloride, a moderate corrosive, and potassium dichromate, which is weakly to negligibly corrosive. The tests were made in 1 normal solutions at room temperature for a 48-hour period following a 48-hour previous exposure. The spray test was run for 30 days.

TABLE 285.—*Copper vs. Salt Solutions.*

Condition	Mg. per sq. dm. per day	
	Sodium Chloride	Potassium Dichromate
Total immersion		
Quiet	16	1.7
Air-agitated	29	.3
Alternate immersion		
Continuous	17	.5
Intermittent	6	1.1
Spray (30 days)	3.5	<.3

Aeration and agitation is seen to be rather strongly accelerating in the case of chloride. In fact, a 3% sodium chloride solution under strong aeration and agitation conditions has given a rate as high as 75 mg. per sq. dm. per day in three day exposure.⁴⁴ Aerated calcium chloride brine (1.14 spec. grav.) at room temperature has given a rate of 150 mg. per sq. dm. per day for copper, in a 24-hour test.⁴⁴ The chlorides of potassium, sodium, magnesium and calcium are substantially alike in the order of their attack.^{11, 14, 16, 33, 41, 43, 51, 55} Where reacting acid, solutions become

more corrosive, with aeration becoming an accelerating factor. Zinc chloride and aluminum chloride solutions are examples.

The salts that have negligible attack on copper—1 mg. per sq. dm. per day and less—include the sulfates and nitrates of sodium, potassium, magnesium, calcium, etc.^{11, 14, 55} The alkali carbonates and other salts reacting alkaline^{11, 13, 41, 43} are likely to corrode at rates two or three times this maximum. The hypochlorites, except in very dilute solutions,⁴¹ are strongly corrosive.⁵¹

Ammonia salts in moderate concentration yield rates of 15 to 80 mg. per sq. dm. per day, perhaps higher under strong aeration and agitation conditions.

Solutions of the oxidizing acid salts—ferric and cupric, mercuric, stannic and silver salts,—are strongly corrosive to copper with rates ranging above 100 mg. per sq. dm. per day, often much higher. This is particularly true of the chlorides.

Cyanides are strongly corrosive to copper.

FOOD PRODUCTS

Copper is a standard material in the construction of equipment used in the preparation of foodstuffs, e. g., kettles, evaporators, pasteurizers, containers, and sheet metal work. The resistance of copper to foodstuffs is such that copper equipment ordinarily has an indefinitely long life, and under conditions where the food product is held for a brief period only—less than an hour or two—in contact with the metal, and where the metal can be cleaned frequently and periodically, copper is reasonably satisfactory. It has become common practice to coat the inside surface of copper equipment with tin. In spite of the fact that a tin coating is not permanent, this practice has its advantages. It prevents the formation of unsightly salts and the discoloration of the product, in cases of prolonged exposure. Again, copper is a rather rapidly tarnishing metal in both atmospheric and submerged exposure, whereas tin is not.

The subject of the toxicity of copper salts has been in a confused state principally because of the failure to distinguish between the effect of heavy doses of copper compounds and of the relatively minute proportions normally absorbed from copper equipment. Investigations^{48, 21} strongly indicate that small quantities of copper are definitely beneficial to life. This is not a surprising discovery—though an extremely significant one—in view of the fact that most foods carry naturally an appreciable copper content,^{37, 49, 82} e. g. (typical analyses) cow's milk 5.0 p.p.m., woman's milk 0.4-0.6 p.p.m., potatoes 1.9 p.p.m., asparagus 7.0 p.p.m., walnuts, 11.2 p.p.m. oats 6.5 p.p.m., egg yolk 1.8 p.p.m., oysters 800 p.p.m. The occasional toxicity of oysters is not considered to derive from the copper. It would be

expected that the processes of the human body would be adjusted to this constant environment of copper in foods.

A comparison between the quantity of copper naturally present in milk and the quantities absorbed from processing equipment is given in Tables 286 and 287.⁴⁶

TABLE 286.—Copper Content of Milk.

Milk	
Raw	0.43 p. p. m.
Screened (copper screens)	0.45 p. p. m.
Screened (copper screens had stood exposed to air for 5 min. between loads)	0.97 p. p. m.
Condensed Milk	
Skimmed milk condensed to 36% total solids in copper vacuum pans	3.7 p. p. m.

TABLE 287.—Copper Content of Fruit Products Commonly Processed in Copper Equipment.

Plant 1		Plant 3	
	p.p.m.		p.p.m.
Strawberry preserves	4	Plum jelly	55
Blackberry preserves	4	Strawberry jelly	60
Cherry preserves	3	Raspberry jelly	80
Apple butter	3	Raspberry preserves	45
Chili sauce	7	Apple butter	110
Ketchup	8	Chili sauce	18
Plant 2		Plant 4	
Currant jelly	7	Raspberry jelly	2
Raspberry jelly	5	Raspberry preserves	7
Raspberry preserves	4	Peach preserves	4
Peach preserves	6	Strawberry preserves	9
Strawberry preserves	10	Blackberry preserves	4
Blackberry preserves	3	Pineapple preserves	3
Apple butter	24	Plum preserves	6
Grape jam	4	Apricot preserves	11
Chili sauce	8		
Ketchup	12		

Where food processing ordinarily involves only short periods of contact between product and metal equipment, the cases where copper absorption may approach toxic significance are undoubtedly rare, corrosion rates being ordinarily low.

Data suggesting the order of attack of copper in certain food products are given in Tables 288 to 291.

Hot to boiling fruit juices have given rates of 1 to 10 mg. per sq. dm. per day on copper,^{8, 53} and in one set of data⁴⁴ the rates in Table 288.

TABLE 288.—Copper vs. Fruit Juices.

	Temp. ° F.	Pressure Mm.	Time Hours	Mg. per sq. dm. per day
Orange juice	113	60	1/2	44
	203	760	6	24
Lemon juice	113	60	3/4	97
	203	760	6	12
	113	60	1	23

Tomato products may be mildly to strongly corrosive, depending on conditions. Plant tests have given the results in Table 289.⁴⁴

TABLE 289.—*Copper vs. Tomato Products.*

	Mg. per sq. dm. per day
Tomato juice in tank after extractor; 170° F.; mild agitation and high aeration; 8 hrs. 50 min.	209-402
Tomato juice filler bowl; 195° F.; very mild agitation; moderate aeration; 9 hrs. 30 min.	133-412
Tomato scalding tank; 200° F.; vigorous agitation; moderate aeration; 7 hrs. 25 min.	78-184
Catsup boiling tank; 220° F.; vigorous agitation; aeration moderate; 7 hrs. 55 min.	22- 43
Catsup finisher; 210° F.; slight agitation; intermittent exposure to air; 6 hrs. 50 min.	24-108

Whereas cold milk has low to negligible action on copper—1 to 10 mg. per sq. dm. per day,⁴⁴—the action of agitated aerated milk at room temperature becomes moderately corrosive—15 to 35 mg. per sq. dm. per day.^{29, 31, 44, 60} At pasteurizing temperature and higher corrosion becomes severe—85 to 150 mg. per sq. dm. per day,^{29, 31, 60, 71} with higher rates under strong agitation conditions.

A thorough investigation of corrosion rates in condensed milk and evaporated milk plants⁶⁹ has given the rates in Tables 290 and 291 for copper.

TABLE 290.—*Copper vs. Milk Products.*

Exposure in Evaporator	Mg. per sq. dm. per day	
	Condensed	Evaporated
Bottom	6-26	6-58
Middle	8-25	8-45
Top	4-28	7-72

TABLE 291.—*Copper vs. Milk Products.*

Exposure	Mg. per sq. dm. per day	
	Condensed	Evaporated
Drop tank	10-21	14- 35
Milk storage	0	0- 4
Hotwell	43-78	35- 56
Preheater	—	123-160
Fluid milk storage	3	—

WATERS

Copper has a generally admirable resistance to all types of fresh waters.^{12, 66, 67} As a result copper is commonly used for such purposes as water lines, domestic hot-water tanks and linings on wooden storage tanks, and heat exchangers. Actual rates of corrosion are low, as a rule negligible. Perhaps in most exposures the rates would be around 1 to 5 mg. per sq. dm. per day and less. Copper is not satisfactory for distilled water con-

tainers, not because the life of copper is short but because the purity requirements of distilled water are exceptionally high. The action is barely sufficient that in several months exposure copper will acquire a loose thin layer of corrosion product. Beneath this layer shallow pitting sometimes develops after long exposure.

Carbonated water becomes much more corrosive. Twenty-hour tests made at room temperature in water saturated with air and carbon dioxide gave rates of 10 to 67 mg. per sq. dm. per day in the case of city water, and 13 to 40 in the case of distilled water.⁴⁴

As a resistor for sea water copper is probably the most useful of metals, although there is definite slow corrosion. At one time it was common to sheathe boat bottoms with copper; this is still being done to a limited extent. The principal drawback lies in the tendency copper has to corrode locally under specific conditions; (a) where there is a rapid flow of solution past the metal, (b) where stagnation encourages the formation of concentration cells, as at stagnant waterlines. Copper is far from efficient as a condenser tube material, in steam power plants, because of rapid corrosion at the velocities of flow commonly involved.

Even though sea water is much more corrosive to all metals than fresh water copper, as stated, is valuable in widespread marine usage. Rates range from around 1 mg. per sq. dm. per day under the mildest conditions—quiet submersion and low degree of aeration—to 60 to 70 mg. per sq. dm. per day under the more difficult conditions. Velocity becomes a very important accelerant along with aeration, particularly if the water is in rapid movement over a localized area. It is this condition that exists within condenser tubes handling sea water, a condition for which years ago copper had been found unsuitable.

In one series of tests² that ran for 10 years, an average corrosion rate of 2 mg. per sq. dm. per day was obtained, with a maximum of 8 mg. per sq. dm. per day at localized areas. The specimens were copper tubing, held horizontally, with sea water in constant gravity flow through them. In other tests copper specimens submerged $8\frac{1}{2}$ years in agitated, moderately aerated sea water were corroded at rates of 1 to 7 mg. per sq. dm. per day and less.

In another long-time test²³—4 years—copper bars were exposed in Bristol (England) Channel at a position where they were submerged 93% of the time. The corrosion rates were about 15 mg. per sq. dm. per day, with no appreciable localized attack. In another series of tests, over a three-year period, bars of copper exposed at half-tide level in Southampton (England) Harbor gave rates on the order of 0.5 mg. per sq. dm. per day.²⁵ In this latter test a heavy accumulation of mud and oil was believed to have been protective.

Impingement tests with sea water have led to extremely strong corrosion of copper.⁶ A water stream carrying entrained air impinging at a velocity of 10 ft. per second at various angles penetrated copper specimens at rates of .048-.15 in. per year (300 to 940 mg. per sq. dm. per day) at localized areas. This impingement condition is aggravated as compared with ordinary condenser tube conditions, but these rates are an indication of the intensity of concentration cells set up by differential velocity.

An important factor in connection with sea water behavior is that barnacles and sea-life do not collect on copper as they do on metals not rich in copper. Copper salts resulting from normal corrosion have a toxic effect on the organisms. This property is of great value in keeping copper clean in marine use and makes it a most useful constituent of antifouling marine paint.

ATMOSPHERE

Copper is more generally used by far in outdoor atmosphere conditions than any other metal requiring no protective coatings. Typical applications are electrical transmission, telephone, telegraph and trolley wires, window screening, and architectural sheet metal work, as roofing, flashing, spouting. Many are the cases where copper has endured for centuries and the expectation of life is often measured in generations rather than years.

In atmospheres carrying even only traces of gaseous sulfur compounds (hydrogen sulfide, sulfur dioxide) copper normally tarnishes, the rate of tarnishing increasing with the sulfur compounds. In the absence of sulfur compounds, copper tends to remain untarnished. In industrial and semi-industrial outdoor exposure the tarnish on copper develops into a pleasant-appearing black to green corrosion product that is common on the roofs, flashing and spouting of city buildings. The green patina which has a very definite esthetic value, develops slowly, sometimes over a period of years. In city atmosphere the green color is due largely to the basic sulfate.^{73, 74} The basic chloride and carbonate are often present.

These evidences of corrosive action do not reflect a condition of serious penetration of the copper. At least some of the corrosion products are protective. General experience and actual tests point to penetration rates in city atmospheres of around 0.1 to 2 mg. per sq. dm. per day, in rural atmospheres perhaps one-tenth of this range. A hundred years or more would therefore be required before a sheet .030 inch thick would be penetrated in city exposure; it is likely that penetration rates over long periods of time are considerably lower than 1 mg. per sq. dm. per day. Vernon and Whitby⁷⁴ have examined metal removed after 300 years of service.

Very highly sulfidizing^{72, 79} atmospheres, such as in the neighborhood of railway roundhouses, in railway tunnels, etc., are more corrosive to

copper, in fact at times these are rapid in their attack—on the order of 60 mg. per sq. dm. per day—and the attack is often of a pitting nature.

The results in Table 292³⁹ indicate the order of penetration rates of copper in exposure to different atmospheres, and compare the behavior of pure copper and arsenical copper. The duration of the tests was one year, and three criteria of damage were used. The specimens were exposed outdoors, those giving weight increase results being protected from the wash of rain and from dust accumulation, the others being exposed freely to the rain.

TABLE 292.—*Copper vs. Outdoor Atmosphere.*

Atmosphere	Mg. per sq. dm. per day		
	Weight increment method	Resistance method	Loss in weight method
Rural			
Pure copper098	.85	.47
Arsenical09	1.2	.39
Suburban			
Pure copper23	1.5	.71
Arsenical22	1.6	.60
Mild industrial			
Pure copper25	2.3	.96
Arsenical30	2.2	.87
Urban			
Pure copper71	1.9	.97
Arsenical78	2.2	.96
Marine			
Pure copper24	2.4	.91
Arsenical27	2.3	.77

Using loss in tensile strength of wires as a criterion of behavior, the same investigator, Hudson,⁴⁰ calculated the average corroded layer of metal as .00018 to .00026 inch per year for “high conductivity” and arsenical copper. These correspond to 1.1 to 1.6 mg. per sq. dm. per day average attack. The specimens were in free open exposure in South Kensington (England), the duration being two years.

Friend²⁴ reports rates of .46 to .63 mg. per sq. dm. per day for seven-years exposure of copper in Birmingham (England) atmosphere.

An example⁴ of accelerated corrosion is the case of the penetration, in 16-years exposure to industrial atmosphere, of .021 inch copper flashing; the penetration occurred in narrow bands at the edge of overlying shingles, the remainder of the metal surface being in good condition. The accelerated corrosion (8 mg. per sq. dm. per day, localized) was due perhaps to a concentration cell of which one element was moisture held stagnant by capillarity beneath the edge of the shingles, and the other an adjacent area of moisture in relative motion.

HIGH-TEMPERATURE CONDITIONS

While copper has certain desirable properties in resisting oxidation at temperatures of some elevation, it is not considered a high temperature metal; its strength and its resistance to hot atmospheres are low compared with iron and steel, and iron-chromium-nickel.

Exposed to pure air copper acquires an oxide coating at normal room temperatures, as Vernon⁷² has pointed out, and the coating that forms is protective in the sense that it increases in thickness at a decreasing rate with time. This relationship holds essentially throughout the range from room temperature to 1850° F., the rates increasing with temperature.

The behavior of copper in oxygen at 932° and 1832° F. is indicated in Figures 63 and 64, according to tests by Pilling and Bedworth.⁵⁸

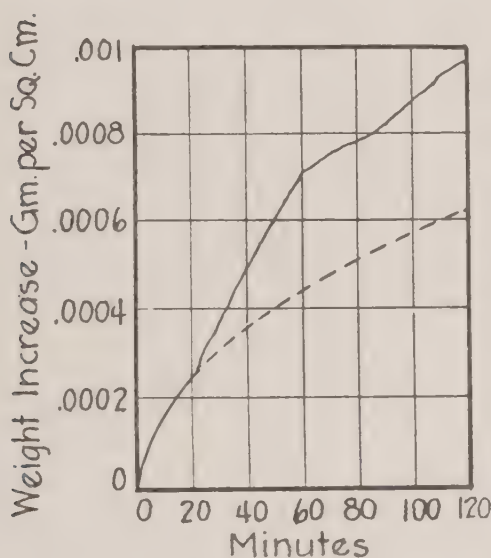


FIGURE 63. Copper vs. Oxygen at 932° F., Continuous Oxidation Curve.

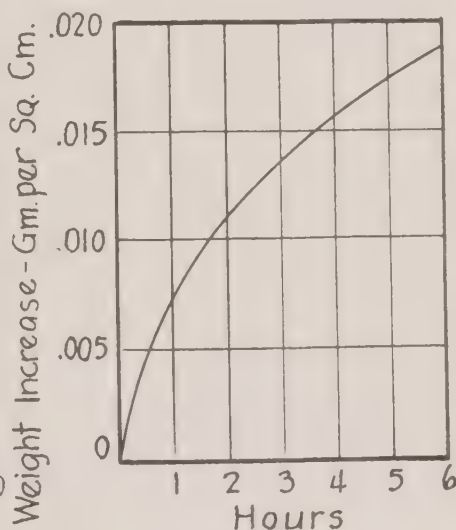


FIGURE 64. Copper vs. Oxygen at 1832° F.

Among the conclusions of Pilling and Bedworth are the following:

1. The high temperature oxidation of copper is a direct reaction between copper and oxygen. Water vapor, if present, is inert.
2. Oxygen pressure affects oxidation in two distinct ways: (a) above 0.3 mm. the rate of oxidation increases slowly with pressure; (b) below 0.3 mm. the rate increases rapidly with pressure.
3. The oxide layer is composed almost wholly of cuprous oxide. The characteristics above outlined are indifferent to the presence of cupric oxide as a thin surface film.

Reducing gases such as hydrogen, carbon monoxide, and hydrocarbons have an embrittling effect⁵⁷ in the high temperature range on un-deoxidized

copper, normally carrying on the order of 0.03 to 0.08% of oxygen as cuprous oxide. Gases like hydrogen and carbon monoxide reduce the oxide and form water and carbon dioxide respectively. Since hydrogen diffuses faster in copper than water vapor, and carbon monoxide faster than carbon dioxide, the reaction results in an increased volume that causes embrittlement.

The embrittling action of reducing gases ⁸¹ increases in severity with the oxygen content of the metal and the temperature. Bassett and Bradley ¹ have pointed out that the depth of deoxidation of copper heated in reducing gas is greater the less cuprous oxide originally present, at least within the range of .015 to .136% oxygen.

Moore and Beckinsale ⁵⁴ have observed that the effect on copper with 0.07% oxygen begins to be important at 1112° F.

Fuller ²⁶ has explained the embrittlement of copper heated at 1472° F. one hour in an iron pipe filled with sea-sand as due to reducing gas formed by carbon in the pipe and organic matter in the sand. The reduction of oil films on heating has the same effect.

MISCELLANEOUS CORROSIVE SUBSTANCES

Sulfur compounds. Sulfur and sulfur compounds have a strong tendency to corrode copper. Against compounds in which the sulfur content is low, such as gasoline, the action is confined to tarnishing without appreciable penetration.^{65, 78, 80} Advantage is made of the tarnishing of copper by sulfur-bearing compounds in gasoline in a test for determining the corrosiveness of gasoline. In this, a fresh copper strip is immersed in gasoline at 122° F. for three hours, and if the copper tarnishes, the gas is considered too corrosive for use in cars. The results in Table 293 indicate the quantities of free sulfur that have a tarnishing effect.

TABLE 293.—*Copper vs. Gasoline.*

Sulfur %	80° F.	122° F.	212° F.
.06	Medium black	Heavy black	Heavy black
.05	Black spots	Medium black	Heavy black
.04	Fine black spots	Black spots	Medium black
.03	Fine black spots	Fine specks	Black spots
.02	Slight discoloration	Discoloration	Discoloration
.01	Unchanged	Unchanged	Slight discoloration
.00	Unchanged	Unchanged	Unchanged

An example of the action at room temperature of sulfur compounds is the case of a "plastilin" mixture carrying 16% free sulfur and 28% fatty acid held against samples of copper. In 7 days the rate at 65° F. was 49 mg. per sq. dm. per day; at 86° to 104° F. the rate of 128 mg. per sq. dm. per day. The specimens were pitted beneath a black coating.³

Molten sulfur is extremely corrosive, the rate in 5 hours at 284° F. being, in one case, as high as 9,400 mg. per sq. dm. per day.³ Boiling sulfur is extremely corrosive. A test is recorded³⁶ where a copper rod $\frac{3}{8}$ inch in diameter was completely dissolved in 4 hours—a rate of 2,000,000 mg. per sq. dm. per day.

Chlorinated hydrocarbons. Cold carbon tetrachloride is only very weakly corrosive to copper, with rates around 1 mg. per sq. dm. per day. In hot carbon tetrachloride copper corrodes at relatively high rates in the presence of air and at low rates in the absence of air. The corrosive power of the tetrachloride is due to the presence of hydrochloric acid, formed by hydrolysis. Exposed in the vapors of a boiling mixture of tetrachloride and water for 100 hours, the rate for copper was 18 mg. per sq. dm. per day. In this test there was virtual exclusion of air.⁶¹ In another test of 22 hours duration, a vapor and air mixture gave a rate of 116 mg. per sq. dm. per day.⁴⁴

Other tests in the tetrachloride and other chlorinated solvents have given the rates in Table 294.⁴⁴ The specimens were partially immersed in the solvents, in one case with a water layer, in the other without.

TABLE 294.—*Copper vs. Chlorinated Hydrocarbons.*

	Mg. per sq. dm. per day			
	Room Temp.		Boiling	
	Water Layer	No Water Layer	Water Layer	No Water Layer
Carbon tetrachloride	4	.2	873	.3
Chloroform7	.5	65	47
Ethylene dichloride	1	.2	73	9
Trichlorethylene	6	.2	38	—
Mixture of tetrachloride and trichlorethylene	2	.1	1078	2.5

The presence of water is seen to have been necessary for heavy corrosion to take place.

Ten-hours exposure in boiling chlorinated hydrocarbons gave rates as given in Table 295. The liquids carried seeds (moisture) in one case and no seeds in another.⁶⁴

TABLE 295.—*Copper vs. Hydrocarbons.*

	Mg. per sq. dm. per day	
	With Seeds	Without Seeds
Carbon tetrachloride	180	360
Dichlorethylene	<7	<7
Trichlorethylene	150	<7
Tetrachlorethane	650	1100
Pentachlorethane	<7	440

Further tests showing the corrosive action of trichlorethylene are given by Carlisle and Levine.¹⁰

Molten metals.³⁴ Copper is not a satisfactory material for handling molten metals—tin, zinc, bismuth, antimony, lead.

COPPER

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Chapter XX

High-Copper Alloys—Brass, Bronze, Nickel Silver

The broad usefulness of pure copper is expanded and magnified by the high copper alloys which, often with no serious diminution of corrosion resistance, add to its properties a strength comparable with some steels. The bronzes—copper alloyed with tin, cadmium, silicon, aluminum and other elements—, and the brasses—copper alloyed with zinc—, have evolved as strong varieties of copper.

As a group the high copper alloys behave in corrosion much like copper. In the most important exposure, atmospheric, no virtual difference exists between copper and the bronzes in having extremely high resistance. The brasses, though somewhat inferior to copper and the bronzes in the atmosphere, are useful as a cheaper variation and because of special working properties. In sea water, another condition the copper group is very widely called upon to handle, copper is better under some conditions and the bronzes and brasses under others.

Bronze, as a term, was applied originally to copper-tin alloys. Those with tin contents up to 10% continue to be the most important group. The casting variations often carry zinc and lead. Two typical and widely used casting alloys are 85 Cu 5 Sn 5 Zn 5 Pb and 88 Cu 10 Sn 2 Zn.

Perhaps the strongest of the bronzes are aluminum bronze, the aluminum running up to 10% with and without iron and nickel, and the 96 Cu 3 Si 1 Mn type of alloy. Intermediate in strength between these and copper are the various alloys with 98 to 99% copper and small contents of elements like silicon and cadmium. This group developed to answer the need of a stronger material than copper and yet with a good share of the high electrical conductivity of copper.

The copper-zinc alloys range from the low brasses with 10, 15 and 20% zinc through 70 Cu 30 Zn and 66 Cu 33 Zn to 60 Cu 40 Zn. A tin addition of 1% to the 60 Cu 40 Zn and the 70 Cu 30 Zn is made for the sake of better behavior in sea water. The 60 Cu 40 Zn is modified in casting form with small additions of iron, manganese, aluminum and nickel (the "manganese bronzes") for markedly better strength and hardness. Lead is added to a number of compositions for better machinability.

The use of the nickel silvers has developed because they add to the desirable corrosion resistance and mechanical properties of the copper-zinc alloys an appealing white color. They are capable of being polished themselves to a beautiful finish or to serve as a base for silver or other surface plating. These carry up to 30% nickel in a brass mixture. Their principal uses are for table flat-ware, restaurant and soda fountain sheet metal work, in plumbing fixtures, and casting work in food processing plants and in miscellaneous stampings and wire products.

The copper alloy group have reasonably good resistance to acid solutions, provided the oxidizing capacity of the solution is not high. They ordinarily are not the best-suited metals for handling alkaline solutions, but against neutral salt solutions and waters, both fresh and sea, they are very widely used. They are moderately satisfactory with food products. Great resistance to the atmosphere and waters accounts for the larger part of their utility as corrosion-resistant metals.

TWO-METAL GALVANIC BEHAVIOR

The copper alloys, like copper, are cathodic to iron and steel, aluminum, lead, tin, and zinc, and to the chromium alloys when in their active condition. Nickel often is anodic to copper, but accelerated corrosion usually is not pronounced in the milder exposures. Nickel-copper is so close to the bronzes electrochemically that it is apt to alternate polarity. On the other hand the bronzes are in most cases anodic to nickel-copper.

Brasses and aluminum bronze are closely similar in electrochemical behavior, and both are definitely anodic to copper and the high copper bronzes. In active corrodents galvanic acceleration with such couples would be recognizable.

The results of one test on galvanic behavior are worth mentioning.³³ With a strong solution of quiet sodium chloride as the electrolyte, the polarity in open circuit was determined for several combinations of copper alloy couples. No current was found to flow in any combination, on closing the circuit, indicating that accelerated corrosion was either absent or extremely low.³³ (See Table 296.)

TABLE 296.—*Copper Alloys—Galvanic Behavior.*

Cathode	Anode	Volts
Bronze (85 Cu 5 Sn 5 Zn 5 Pb)	Brass (70 Cu 30 Zn)	.013
Copper	Bronze	.035
Copper	Silicon-manganese bronze (96 Cu 3 Si 1 Mn)	.038
Bronze	Silicon-manganese bronze	.002
Silicon-manganese bronze	Brass	.011
Monel (68 Ni 29 Cu)	Bronze	.066
Monel	Silicon-manganese bronze	.048

In acid solutions coupling of different copper alloys is likely to lead to accelerated attack of undesirable intensity.

The coupling of iron and the copper alloys is common enough in equipment handling neutral solutions and waters. Iron is both anodic to bronze and moderately attacked by neutral solutions carrying dissolved oxygen. If such solutions are good electrolytes, like sea water or brines, definite acceleration will occur. Aerated sea water will corrode iron at about 20 mg. per sq. dm. per day. Coupled with large areas of copper alloy the rates might climb two or three-fold. In one case bronze screws were used to attach a bronze tongue to a cast iron centrifugal pump casing, handling sea water. The water washed the assembly at rather high velocity. Within two months the cast iron was severely attacked and the screws were loose due to corrosion of the threads of the iron.

In fresh water, couples of copper alloys, or of a copper alloy with iron are rarely dangerous. Accelerated attack of the iron tends to become noticeable where the area of iron is small and the area of copper alloy great, as in the case of a steel bolt in a copper alloy plate. In aerated waters iron even when uncoupled becomes noticeably attacked.

DEZINCIFICATION

Copper in solution will tend to plate out cathodically on copper-zinc alloys with the equivalent in alloy passing into solution. The greater the concentration of copper ions and the higher the zinc content of the alloy, the greater is the tendency for the copper to plate out. The corrosion of the higher zinc brasses under certain exposure conditions introduces copper ions in sufficient concentration into the interfacial film of solution to bring about deposition of copper. It is this phenomenon that is known as dezincification. The subject has been dealt with in a number of papers,^{3, 4, 8, 9, 19, 20, 47, 52} perhaps most effectively by Bengough and May.¹⁰

Dezincification is not often serious. Brass with zinc ranging from 30 to 40% is widely used as steam-condenser tubing. In sea water, tubes of the 30% alloy frequently have given as much as twenty-years service, and more. Even though these may at times be dezincified the progress of the attack has not been sufficient to destroy the usefulness of the tubes. In fresh waters, tubes of both the 30 and the 40% zinc alloys are very widely used, in a great many cases with success. Brass with 20% zinc has at times suffered serious attack of this type but is definitely more resistant than brasses with higher zinc. The 15% zinc alloy is an improvement over the 20% zinc alloy; in fact the former is considered essentially free from attack under all normal conditions of use.

Brass with 40% zinc is of a two-phase nature, the two constituents being known as *alpha* and *beta*. The *alpha* constituent carries less zinc than the

beta, and consequently is less susceptible to dezincification than the *beta*. Muntz metal with its 40% zinc content and "naval" brass with 39% zinc and 1% tin are both two-phase alloys, and are sufficiently susceptible that for sea water they are seldom considered satisfactory. On the other hand, the "manganese bronzes" carrying approximately the same zinc content are often used in sea water, for such purposes as propeller wheels and other heavy castings. The use of manganese bronze for propellers is dictated by the hardness of the alloy, carrying as it does small contents of iron and sometimes aluminum and other elements. Actually such heavy parts may stand dezincification that would be seriously rapid if taking place on metal of thinner section.

In fresh waters, more particularly of high chlorine content, though not necessarily so, dezincification sometimes takes place with Muntz metal. It has been observed, for instance, with the natural waters of Washington, D. C., Dedham and Brookline, Mass., in sufficient intensity that pipes in households have changed to porous copper through the entire thickness, in 20 to 25 years time. It is not clear whether hard water or soft water is the more reactive.

As stated above two necessary conditions for dezincification are high copper-ion concentration, and high zinc content in the alloy. There is a third condition that has been pointed out by Bengough and May,¹⁰ namely, relatively low degree of aeration. This, strictly speaking, is associated intimately with the copper-ion concentration, since it has been shown that the ingress of dissolved oxygen into the interfacial layer at the surface of dissolving brass leads to precipitation of a copper compound. The consequence of course is a lessening of copper-ion concentration.

Bengough and May have pointed out the extreme complexity of the chemical reactions taking place at the surface of corroding brass. They have distinguished as many as twelve precipitated compounds, all of which may influence the protectiveness of the film that develops on the metal. It is this film, when of a certain nature, that pockets solution sufficiently to let copper-ion concentration build up, and that offers an obstacle to the ingress of dissolved oxygen. Whether the corrosion product film will be of the type to prevent corrosion, or to promote dezincification, or to allow general dissolution without copper deposition can scarcely be anticipated in the present state of knowledge.

A number of observations have been made, in the study of dezincification, that are well to mention here. One is that action sometimes is localized and severely penetrating and at other times generally spread over the surface and of shallow depth. So-called plug type dezincification occurs at times on steam-condenser tubes handling sea water, although why the action takes this form is not clear.

Another fact is that scales high in zinc compounds seem to favor dezincification by being especially resistant to the penetration of oxygen.

The presence of 1% tin in 70 Cu 30 Zn favors resistance to dezincification. Thus, Bengough and May¹⁰ found the appearance of copper deposition on Admiralty metal was delayed for about two months as compared with regular 70 Cu 30 Zn, and furthermore the total amount of deposition was less. Also the presence of .01 to .02% arsenic was found definitely to prevent deposition of copper. The presence of iron and probably manganese favors dezincification.

Dezincification in sea water is intensified by the presence of more cathodic metal in galvanic couple with the brass. Where the cathodic metal is extensive in area the action has been observed to be remarkably rapid.

Dezincification takes place in atmospheric exposure, though at a very slow rate.²⁸ It is apt to become damaging only in the case of thin section metal, such as fine wire. Moist sea coast and urban atmospheres are undoubtedly more conducive than other atmospheres.

Aluminum bronze is subject to attack similar to dezincification, though the action can scarcely be referred to as dezincification. Copper tends to plate out on aluminum bronze, with an 8% aluminum content for instance, as it does on brass. Whether the tendency is greater or less, and whether or not it exists under the same range of conditions, as in the case of brass, cannot be stated. It has been observed a number of times after exposure in warm dilute sulfuric acid, to the depth of three quarters of an inch of rod.

CORROSION CRACKING OF BRASS

Under some corrosive conditions, in which it is otherwise satisfactory, and when proper precautions are not taken, brass of high zinc content may be subject to corrosion cracking, known also as season cracking.^{43, 51} This type of behavior is distinct from corrosion fatigue in that the stresses, which in combination with corrosion lead to corrosion cracking, are of a static nature rather than dynamic or cyclic. Furthermore, the action progresses along grain boundaries.

More study of this phenomenon has been done in connection with brass than with other metals, because the large quantities of brass used under conditions which cause it, have made material for such study available. Corrosion cracking occurs also in other metals.

In the cases where brass is affected by corrosion cracking internal strains imposed by cold working are usually present. Strain-relief annealing, following cold work, can be counted on as a complete preventive of corrosion cracking from such strains. Externally applied stresses may also cause corrosion cracking, and at certain critical values such stresses may result in

corrosion cracking of brass and other metals, whether or not they have been properly annealed.

Although exposure to moist ammonia atmospheres and mercury salt solutions is particularly drastic in producing cracking, exposures as mild as atmospheric will produce it over a period of time. A number of cases are on record where brass has spontaneously cracked under mild conditions as in indoor atmosphere, especially after rapid changes in temperature. On the other hand, a good many other exposures have no effect. Thus tons of condenser tubes of 60 Cu 40 Zn are used in fresh waters and 70 Cu 30 Zn and 70 Cu 29 Zn 1 Sn in salt waters, in the presence of externally applied stress if not cold working strains, without cracking. Acids as a rule do not cause it. Traces of ammonia in the atmosphere are believed to be a potent agency.

Corrosion cracking, like dezincification, is almost unknown in brasses of zinc content below 20%. The two-phase brass compositions, such as 60 Cu 40 Zn, are more susceptible than the one-phase group with less than 33% zinc. Since the two phases respond differently to heat and both hot and cold working forces, it is believed that even uniform treatment of this type may produce unevenly distributed internal strain.⁴² Cracking for the most part takes place in an intercrystalline manner; occasionally in the two-phase alloys cracks have been observed to transgress the *beta* crystals.

A positive test for the presence of the strains which produce corrosion cracking is the characteristically intercrystalline action of mercury salt solution.¹ Corrosion cracking which has been known to affect cartridge cases in atmospheric exposure can be forecast by subjecting typical samples to a four-hour exposure in strong mercury solution.

A common method of preventing corrosion cracking is by annealing work-strained metal at about 500° F. for an hour or so. This treatment will not affect mechanical properties in an important way, and still is sufficient to relieve practically all the unevenly distributed stress. In the case of drawn tubes, Crampton¹⁵ has found it possible to avoid susceptibility of cold-worked brass, by modifications in drawing practice.

CORROSION AND FATIGUE

Copper alloys have been included in the investigations^{32, 38} of "corrosion fatigue," in which specimens were tested in a rotating cantilever beam fatigue machine while the specimens were exposed to a stream of water. Whereas the endurance limit of copper was not altered by the water stream, the endurance limits of various brasses and aluminum bronze were lowered somewhat. The curves of Figure 65 include the air-endurance curve of 7½% aluminum bronze (2.9% iron) having a tensile strength of 90,000 lbs.

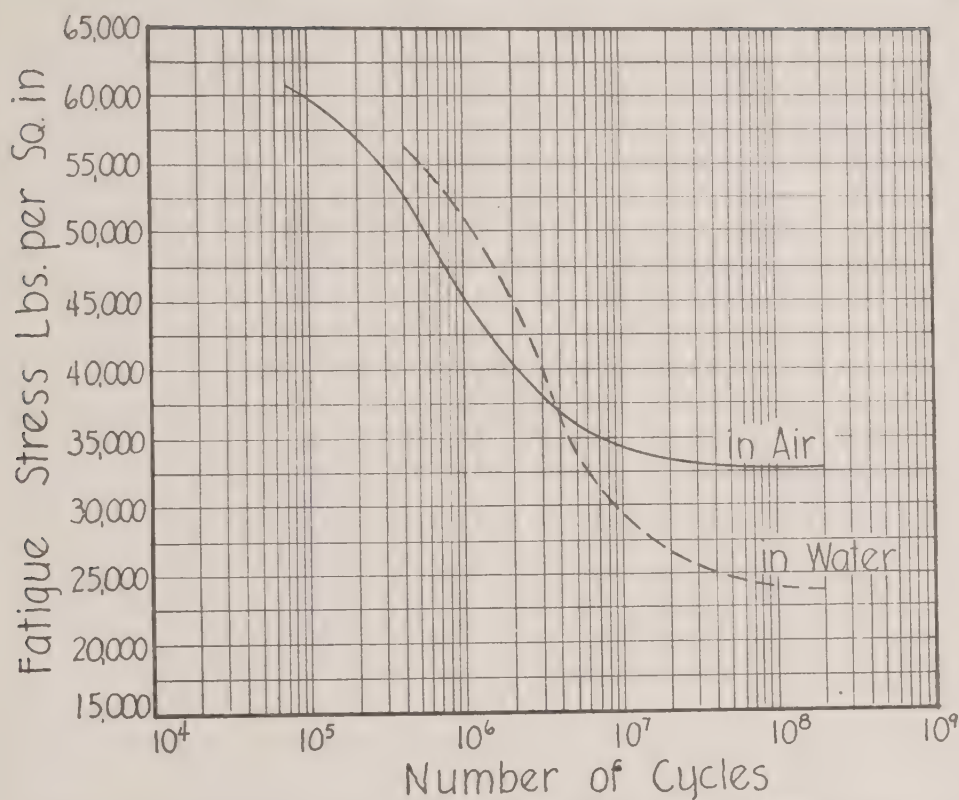


FIGURE 65. Aluminum Bronze vs. Fresh Water in Fatigue (1450 r.p.m.).³⁷

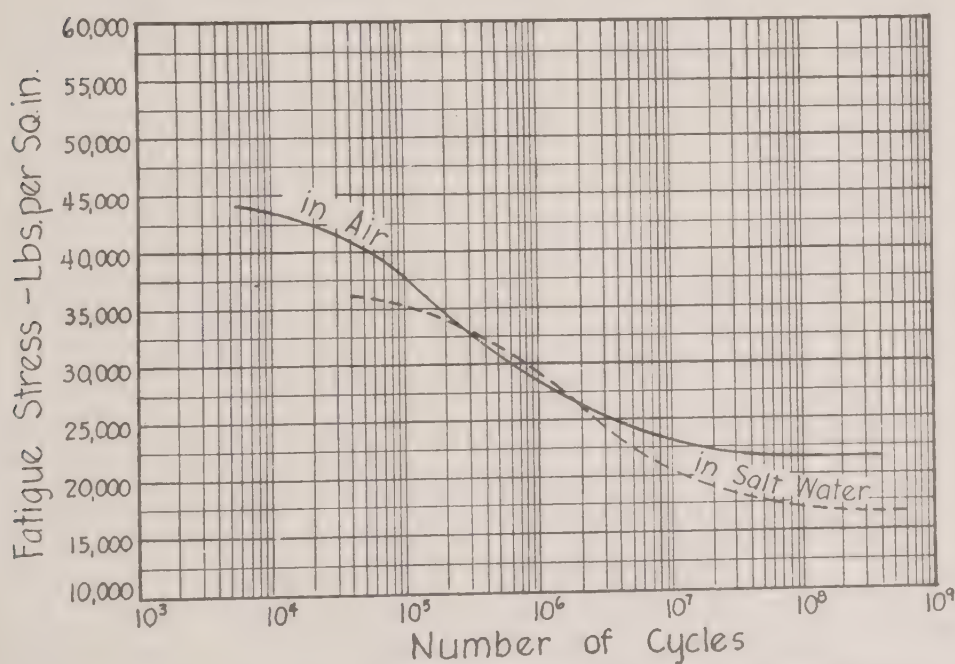


FIGURE 66. Annealed 62 Cu 37 Zn vs. Salt Water in Fatigue (1450 r.p.m.).³⁷

per sq. in., together with results in carbonate fresh water and a saline water. The damage to 62 Cu 37 Zn, both annealed and cold worked, is indicated in Figure 66.

It was also found that,—in common with steels, stainless steels, Monel, and aluminum alloys,—specimens of aluminum bronze suffered a loss in fatigue strength by previous exposure, unstressed, in tap water. The damage corresponded to a 15% drop in fatigue limit from 160 days' previous exposure.³⁸

ACIDS

Against acids the copper alloys behave as a group in much the same way as copper, and the rates of attack of the various kinds of alloys cluster around those of copper. In practically all acid exposure—the principal exception is the very rare case of air-free solution—the rates of attack are definitely appreciable and in many cases moderately high. The corrosion introduces copper ions into the diffusion film against the surface of the metal. All the alloys when corroding have this film carrying copper ions as a common condition. Its presence is in a sense a control over the rate of subsequent corrosion, for the metal-ion solution cells, that are normally associated with such a film, are as important a factor in determining continued corrosion as the oxygen that the solution itself supplies to the reaction.

Several of the alloying elements of copper, besides improving other properties, have a definitely suppressing effect on corrosion in certain conditions. This has been observed with aluminum, zinc, silicon, possibly tin. An unusually good example is given by the data in Table 297⁷ obtained in alternate immersion tests running 216 hours. The tests were of an accelerated nature, and the rates therefore were much higher than would be experienced in simple, quiet-immersion tests.

TABLE 297.—*Copper-silicon Alloys vs. Acids.*

Alloy		Mg. per sq. dm. per day	
Copper	Silicon	10% Hydrochloric room temp.	10% Sulfuric 140° F.
99.31	.57	1500	2680
99.10	.78	1260	2820
98.42	1.14	1060	2430
97.96	1.61	820	1940
97.27	2.12	710	1310
96.45	2.56	640	1430
95.83	3.04	690	1080
96.03	3.17	710	1210
94.60	4.01	760	870

The apparent beneficial effect of zinc additions against hydrochloric and of aluminum additions against several acids is sometimes even more marked. But in these latter cases, where the zinc is present to the extent of 30 to 40%,

the lower rates as compared with copper and other copper alloys are not necessarily indications of a lower degree of attack. Actually the true rates may be fully as high, at times higher, but the deposition of copper from the solution has obscured the fact insofar as weight-loss measurements are concerned. Such dezincification, or "de-aluminification," is a common occurrence with the high zinc alloys of copper and the copper-aluminum alloys in acids. In fact the high zinc brasses seldom are useful with strong acid solutions on account of the tendency to corrode in this fashion.

Leaded bronzes often are considered particularly suited for handling sulfuric acid solutions, a view based on the well-known protective film-forming capacity of lead itself in sulfuric. It is possible that the belief is justified in the case of bronzes with sufficiently high lead, yet the following results in aerated, agitated sulfuric acid would indicate that a lead content of at least 15% has not the desired and expected effect.³³ The tests were run at room temperature for 24 hours. (See Table 298.)

TABLE 298.—*Copper Alloys vs. Sulfuric Acid.*

	Mg. per sq. dm. per day		
	5% acid	15% acid	50% acid
84 Cu 13 Sn 2.5 Zn	250	150	53
75 Cu 11 Sn 15 Pb	360	245	83

Copper itself is often more resistant than its alloys to acid solutions, as indicated by some of the results in Table 299 from tests made on specimens placed in various exposures in the plant of a large chemical company.³³

TABLE 299.—*Copper Metals vs. Acids.*

	Mg. per sq. dm. per day	
	Copper	Brasses Bronzes
Acetic acid		
80% crude, room temp., bottom of tank	35	47- 64
80% pure, room temp., bottom of tank	68	76- 94
80% pure, room temp., top of tank	130	520-650
Formic acid		
90%, 212° F., submerged	240	210-270
90%, 212° F., vapors	36	35-320
90%, room temp., bottom of tank	81	41- 82
90%, room temp., partial immersion	75	55-150
Lactic acid		
30% spent liquor, 80-150° F.	10	94-230
5-48% during concentration in vacuum	43	46- 65

The better resistance of copper is seen to be by no means a consistent fact.

Tin as a rule seems more to be without benefit than otherwise in its effect on copper in acid exposure. Of forty comparisons covering a wide range of acid exposure conditions—dilute, concentrated, aerated, non-aerated, hot, cold—in thirteen cases copper was somewhat better than the tin bronzes and in nineteen cases there was no appreciable difference.

A rather interesting comparison of the possible effect of 1% tin in 70 Cu 30 Zn is given by the data in Table 300.⁸ The specimens were submerged 3 days in quiet .002 normal acid at 122° F.

TABLE 300.—*Copper Metals vs. Acids.*

	Mg. per sq. dm. per day	
	Hydrochloric	Sulfuric
Copper	233	150
70 Cu 30 Zn	214	143
70 Cu 29 Zn 1 Sn	53	33

This result must be used with caution, however, in view of the possibility of dezincification.

An indication of the possible effect of zinc and tin is given by the following set of data comparing copper and 70 Cu 29 Zn 1 Sn in a weakly and strongly corrosive acid respectively, and under both aerated and unaerated conditions.²² The solutions were one normal in strength, and the duration 48 hours following previous 48-hours exposure. (See Table 301.)

TABLE 301.—*Copper Metals vs. Acids.*

Test Condition	Mg. per sq. dm. per day			
	Hydrochloric		Acetic	
	Copper	70 Cu 29 Zn 1 Sn	Copper	70 Cu 29 Zn 1 Sn
Total immersion				
Quiet	320	95	18	20
Air-agitated	5000	3300	65	71
Alternate immersion				
Continuous	3200	1900	35	48
Intermittent	800	350	14	45
Spray (30 days)	290	280	76	110

This concentration of hydrochloric is definitely more corrosive to copper than to the brass, yet here again the possibility of copper cementation on the brass would make this an apparent rather than a real difference. At any rate, of forty-four available comparisons in acid exposure, no appreciable difference between copper and the zinc alloys was evident in ten cases, the zinc alloys were better in sixteen cases, and worse in eighteen.

A review of the data on acid resistance of the copper alloys brings out the interesting point, therefore—and one that is not usually realized—that no marked difference in general resistance exists among the different types. Furthermore, rarely if ever is it true that one type of alloy is better than the others in resistance to a single acid in the various concentration, aeration and heat conditions in which the acid may exist. Differences in resistance among the various alloys are often apparent in any one exposure condition, but these differences are in most cases of minor account, and—a rather important point—almost always unpredictable from experience other than under this very same condition.

In other words it is not possible to predict, with any degree of accuracy, that this or that high copper alloy will be more suitable for handling this or that acid under a given set of exposure conditions. If ever it becomes possible so to predict, it will be because of the accumulation of a far larger body of test data than at present is available, and because the tests yielding the data are far better controlled in the important factors of corrosion than is true of most tests made to date. It appears extremely unlikely that even these developments will bring out a fundamental advantage, in actual use, for any one type of alloy, at least of those developed so far. Corrosion exposure in chemical processing almost never involves the very delicate control of conditions than are required for reproducible results in corrosion testing, and the wider the range of conditions that a given piece of equipment is asked to handle the more nearly alike in behavior the different alloys of which the equipment might be constructed will become.

One circumstance should be mentioned at this point as an exception to this general thesis, and that is the susceptibility of aluminum bronze and high zinc brass to the reprecipitation type of attack. This fact tends to throw these two types of alloy into a somewhat inferior position in acid exposure.

Now will be given a number of sets of data in which various copper alloys were tested under similar conditions.

The rates in Table 302⁴⁶ were obtained in a single solution—vinegar of 4% acetic content—at 68° F. for 100 hours.

TABLE 302.—*Copper Metals vs. Vinegar (Acetic Acid).*

Alloy	Mg. per sq. dm. per day		
	Quiet Immersion	Aerated	Spray
Copper	8	51	200
80 Cu 20 Sn	17	120	140
80 Cu 10 Sn 10 Pb	35	95	115
75 Cu 10 Sn 15 Pb	61	110	150
70 Cu 5 Sn 25 Pb	61	120	620
85 Cu 5 Sn 5 Pb 5 Zn	28	97	140
86 Cu 8 Sn 6 Pb	25	80	115
86 Cu 10 Sn 4 Fe	16	65	170
89 Cu 2.5 Fe 4.5 Al 4 Mn	16	72	206

Tin bronzes with zinc, lead and antimony additions were tested in the acids given in Table 303.¹⁴ The tests were run over an 8-hour period, with constant agitation.

The data in Table 304 are interesting in that they compare phosphor (tin) bronze, silicon manganese bronze, and brass, in acid solutions, cold and hot, aerated and unaerated. The acid was 90% formic, the duration from 7 to 27 days.³³

TABLE 303.—*Copper Metals vs. Acids.*

	Mg. per sq. dm. per day		
	Hydrochloric	Phosphoric	Sulfuric
	6%	5%	5%
89 Cu 7 Sn 4 Zn	1370	310	380
85 Cu 6 Sn 9 Zn	1250	150	440
86 Cu 10 Sn 4 Zn	1310	280	690
82 Cu 10 Sn 7 Zn 1 Pb	1190	290	810
84 Cu 9.5 Sn 6 Pb	1760	320	1180
83 Cu 10 Sn 7 Pb	1600	330	1060
87 Cu 9.5 Sn 3 Sb	1830	260	460
85 Cu 9.7 Sn 5 Sb	1970	340	1060

TABLE 304.—*Copper Metals vs. Formic Acid.*

Alloy	Mg. per sq. dm. per day			
	Room temp.		212° F.	
	Submersion	Partial Immersion	Submersion	Vapors
Copper	81	75	240	36
Phosphor (tin) bronze	57	140	280	36
Silicon-manganese bronze				
Everdur	65	50	205	53
Herculoy	41	78	210	65
Low brass	77	72	230	35
High brass	80	86	240	320

In Table 305³⁴ a large number of alloys were tested in aerated pure 25% phosphoric at 203° F. The duration was indefinitely greater than 24 hours. There is extreme variation in the degree of attack.

TABLE 305.—*Copper Metals vs. Phosphoric Acid.*

Alloy	Mg. per sq. dm. per day
Copper	2100
Aluminum bronze	
87 Cu 7.8 Al 3.7 Fe	1700
89 Cu 8 Al 2.8 Fe	5200 pitting
86 Cu 10 Al 4 Fe	280 "
95.5 Cu 3 Si 1.2 Mn	9300 fine pitting
Brasses	
87.5 Cu 10.5 Zn	140
66 Cu 32.5 Zn	170
60 Cu 39 Zn 1 Sn	430
68 Cu 23 Zn 3 Mn 2 Fe	180
Nickel bronze	
74 Cu 16 Ni 3.7 Fe 5.5 Al	11,000
27 Cu 66 Ni 2.7 Si 2 Fe	1,400
88 Cu 5 Ni 5 Sn	8,000 pitting

Finally, in Table 306, are results comparing two quite unlike alloys under strong aeration and agitation conditions. These illustrate well the relative similarity in resistance of copper alloys, under carefully controlled test conditions.³³ The tests were run 20 hours.

TABLE 306.—*Copper Alloys vs. Acids.*

	Mg. per sq. dm. per day	
	Aluminum bronze	Silicon manganese bronze
Sulfuric		
10%–180° F.	914	1173
25%–180° F.	691	872
Hydrochloric		
3%–160° F.	1423	2460
15%–58° F.	740	677

Nitric acid.^{26, 32} The copper alloys are not useful with nitric, rates running up into the thousands mg. per sq. dm. per day.

Hydrochloric acid.^{7, 8, 14, 22, 26, 30, 32, 33, 35, 39, 48, 53} This is the most corrosive of the non-oxidizing group of acids to the copper alloys. In dilute and moderately dilute concentrations in quiet exposure rates run around 40–200 mg. per sq. dm. per day. Aeration, increasing temperatures, and increasing concentration are strongly accelerating, rates running up over 1000 mg. per sq. dm. per day.

Sulfuric acid.^{7, 8, 14, 26, 30, 32, 33, 35, 39, 48, 53} The copper alloys are fairly resistant to sulfuric solutions, with rates on the order of 10 to 100 mg. per sq. dm. per day in quiet exposure for concentrations up to around 80%. Aeration is strongly accelerating, particularly in the 1 to 20% range of concentration, with rates running up to 100 to 400 mg. per sq. dm. per day. Sulfuric in the pickling of steel has a 5 to 10% concentration and is used moderately hot. Under these conditions, where aeration degree is low, rates run on the order of 100 to 200 mg. per sq. dm. per day, with a two or three times acceleration if the acid should become aerated. Leaded bronzes and aluminum bronzes are used in this service, the latter frequently corroding with cementation of copper.

Acid over 75 to 80% in concentration, particularly when hot, cannot safely be handled with the copper alloys.

Sulfurous acid.^{33, 36} Before the advent of the stainless steels bronzes were widely used for handling acid sulfite and sulfurous solutions. Even now they are used to some extent in sulfurous-sulfuric mixtures that destroy the passivity of stainless. Hot sulfite liquors found in the sulfite process of paper-making corrode bronzes on the order of 1000 mg. per sq. dm. per day and greater. At ordinary temperatures the rates are lower, being on the order of 100 to 200 mg. per sq. dm. per day, perhaps at times higher than this.

Phosphoric acid.^{14, 34, 35, 55} Pure phosphoric in the cold and of low aeration degree is reasonably well resisted by copper alloys, with rates

ranging down below 100 mg. per sq. dm. per day. Higher temperatures are rather strongly accelerating, pushing rates up into the 400 to several thousand mg. per sq. dm. per day range. Crude phosphoric carrying ferric iron is extremely corrosive, particularly when diluted.

Acetic and other hydroxy-acids.^{22, 26, 30, 33, 35, 39, 45, 48} In quiet, room-temperature exposure corrosion rates run around 10 to 100 mg. per sq. dm. per day. Agitation, aeration, and elevated temperatures push the rates up into the 50 to 600 range.

Oxidizers in acid solutions.⁵⁷ Oxidizers like ferric salts, cupric salts, mercuric, stannic salts, etc., are strongly accelerating on corrosion of copper alloys. Such substances, present even in rather low quantities, multiply corrosion perhaps several-fold. Mention has already been made of this in connection with phosphoric; ferric salts are found also in sulfuric-aluminum sulfate mixtures and in acid mine waters. Attack by such substances is likely to be rapid.

Water-line attack. The behavior of aluminum bronze in acid water-line tests has points of interest.³³ The specimens were partially immersed in quiet solutions for ten days at room temperature. In one normal sulfuric large quantities of moist, blue-green salts formed over the unsubmerged surfaces, with a water-line zone of redeposited copper; immediately below this zone the metal was brightly etched, the remainder of the submerged portions being attacked only slightly if at all. In one normal acetic, pale green salts developed though to a less extent than in sulfuric. Pitting occurred at the water-line but no copper deposition, and the submerged surface was lightly etched. In one normal and one-tenth normal sulfurous, corrosion of the pitting type was heavy on both submerged and unsubmerged surfaces, with deposition of copper at the water-line. Water-line exposure should not be considered particularly severe on this alloy nor on copper alloys in general. Due to solution cells that develop, it is corrosive to many metals.

CAUSTIC ALKALINE SOLUTIONS

Copper alloys, like copper, are useful with caustic alkaline solutions in spite of their indifferent resistance to them.^{2, 14, 35, 39, 53} At ordinary temperatures in quiet exposure rates range around 1 to 10 mg. per sq. dm. per day; agitation, aeration and higher temperatures push rates up to 20 to 50 mg. per sq. dm. per day.

An indication of behavior of the high copper alloys can be gained from the data in Table 307 on a brass composition and on copper itself²² in one normal sodium hydroxide. The tests were made at room temperature for a duration of 48 hours following previous 48-hours exposure. The spray tests ran 30 days.

TABLE 307.—*Copper Metals vs. Sodium Hydroxide.*

Condition	Corrosion Rate		
	Mg. per sq. dm. per day	70 Cu 29 Zn 1 Sn	
Total immersion	Copper		
Quiet	14		15
Air-agitated	20		33
Alternate immersion			
Continuous	29		54
Intermittent	14		24
Spray (30 days)	2		1

Although no specific data are available to make it certain, the nickel-silver alloys probably have better resistance than the other metals of the group, against caustic alkaline solutions.

AMMONIUM HYDROXIDE

These alloys like copper are very rapidly attacked by ammonia solutions.^{14, 22} In fact it is well to keep the brasses, bronzes, and nickel silvers away from ammonia conditions of any nature. Cold-worked brass of high zinc content that has not had a suitable strain-relief anneal is susceptible to corrosion-cracking in exposure to moist atmosphere carrying even small contents of ammonia.

The rates in Table 308 were obtained in moderately dilute ammonia solutions. The tests ²² were made at room temperature over a 48-hour period following previous 48 hours exposure. The spray test ran 30 days.

TABLE 308.—*Copper Metals vs. Ammonium Hydroxide.*

Condition	Corrosion Rate		
	Mg. per sq. dm. per day	70 Cu 29 Zn 1 Sn	
Total immersion	Copper		
Quiet	160		95
Air-agitated	430		570
Alternate immersion			
Continuous	870		1400
Intermittent	205		220
Spray	35		21

SALT SOLUTIONS

The copper alloys are widely used handling salt solutions^{14, 31, 39, 40} of various kinds, particularly those that react neutral in aqueous solutions. Among these are soluble nitrates, sulfates, chlorides of sodium, potassium, magnesium and calcium. Corrosion rates in these range around 1 mg. per sq. dm. per day, perhaps somewhat higher in agitated, aerated exposure and somewhat lower in quiet. The chlorides are more corrosive than the other salts, especially under strong agitation and aeration conditions where metal-ion concentration cells become active. Thus a silicon-manganese bronze

was attacked at a rate of 60 mg. per sq. dm. per day in air-saturated, agitated, two-day exposure in 3% sodium chloride.³³ Against chlorides the brasses are definitely better than the non-zinc alloys of the group. A comparison between copper and 70 Cu 29 Zn 1 Sn is given in Table 309. The high copper bronzes are rather similar in behavior to copper itself. These tests²² were made at room temperature, over a 48-hour period, following previous 48-hours exposure. The spray tests ran 30 days.

TABLE 309.—Copper Metals vs. Sodium Chloride.

Condition	Corrosion Rate Mg. per sq. dm. per day	
	Copper	70 Cu 29 Zn 1 Sn
Total immersion		
Quiet	16	11
Air-agitated	29	11
Alternate immersion		
Continuous	17	8
Intermittent	6	3
Spray	3.5	4.5

On the other hand the high zinc brasses (30 to 40% zinc) are susceptible at times in chloride exposure to dezincification.

Ammonia salt^{35, 54} solutions are strong in their action on these copper alloys, and cannot usefully be handled with them. This is particularly true of the chloride. Rates range around 50 mg. per sq. dm. per day in quiet exposure and much above this when strongly agitated.

Of the alkaline salts, the carbonates¹⁴ are reasonably well resisted, rates apparently remaining below 20 mg. per sq. dm. per day. The alkaline silicates, phosphates, dichromates, etc., have slight if any action. With these the expected action of the alkali is suppressed by the formation of silicate, phosphate, dichromate films. Exposure in dichromate, aerated and unaerated,²² has given rates of 1 mg. per sq. dm. per day and less.

The alkaline hypochlorites and cyanides on the other hand are not usefully handled with the copper alloys, rates ranging up over 100 mg. per sq. dm. per day.

Acid salts such as aluminum chloride act like the corresponding acids and are mildly to strongly corrosive when agitated and aerated. Salts that are oxidizing as well as acid are strongly corrosive. Thus the soluble ferric, stannic, mercuric, cupric, and silver salts are better not used with the copper alloys. Rates under average conditions would range above 100 mg. per sq. dm. per day, often well above this. Mercuric salts cause rapid corrosion cracking of high zinc brasses carrying internal strains, as mentioned earlier.

A set of experiments³³ has been made with aluminum bronze specimens partially immersed for eleven days in quiet one normal solutions of various salts. In magnesium chloride a greenish corrosion product accumulated at

the water-line; in sodium carbonate the corrosion product was more pronounced, with pitting at the water-line; in aluminum sulfate pitting occurred at the water-line and below; and in ammonium chloride numerous broad water-line pits occurred. Water-line exposure of course favors concentration cell action on most metals.

FOOD PRODUCTS

Brass, bronze and nickel silver are widely used in handling food products, for such equipment as valves, fittings and pipe lines, pump parts, screens, filters, fastenings. The advantages of these metals lie in the avoidance of the rusting of iron parts, low cost as compared with most other non-rusting metals, and reasonably good resistance to the products. Disadvantages include the accumulation of unsightly green corrosion product on the metal, possible discoloration of the foodstuff, and fear of copper absorption in toxic quantity by the foodstuff. Often, and very successfully, the copper alloys are coated heavily with tin as a preventive of these undesirable features.

The nickel silvers have an appearance advantage over the brasses and bronzes, and often a somewhat better resistance to tarnishing and green salt accumulations. These, in common with the other copper alloys, are subject to blackening by sulfur-bearing foodstuffs, such as some vegetable products.

Actual corrosion rates in food product exposure are usually low to negligible—around 1 mg. per sq. dm. per day and less for the neutral substances, 1 to 20 more or less for acid products like cold milk and fruit juices, and somewhat higher for these under the more severe conditions of aeration or heat.^{11, 16, 30, 45, 53, 59}

WATERS

Corrosion rates of the copper alloys in natural fresh water^{13, 25, 56} are in general low to negligible. Perhaps 1 mg. per sq. dm. per day would be a fair rate for average conditions, which would include quiet exposure and waters in moderate flow or agitation. These compare with average rates for iron of 10 to 20 mg. per sq. dm. per day and higher. Precipitation of salts from waters is more than likely to act in a protective manner. Tremendous tonnages of copper metals in the form of pipe, fittings, valves, etc., are used handling fresh waters—brasses, tin bronzes and silicon-manganese bronzes and copper itself as wrought metals, and the high copper bronzes with tin, zinc and lead as castings. Nickel silver both wrought and cast is used in plumbing where appearance is considered particularly desirable.

High zinc brasses in certain types of waters, notably chloride and hard⁵¹ waters, are susceptible to slow dezincification. As an example, in the course

of years brass pipe handling household water supplies in the suburbs of Boston, and in Washington, D. C., has become locally or completely dezincified. In this condition, though the pipe may retain its physical form, water will soak slowly through the walls of the pipe and any degree of internal pressure will cause failure.

Dissolved oxygen is an important factor in determining the extent of attack of waters on brass. In tests quoted by Speller,⁵⁸ brass was found to corrode in a hot city water with its normal content of dissolved oxygen about ten times as rapidly as in the same water with most of the dissolved oxygen removed. Furthermore dezincification was much more rapid in the presence of the oxygen.

Waters having this action on brass are better handled by low zinc brass (15 to 20% zinc) which is not susceptible to dezincification, or by copper itself.

Sea Water.^{8, 9, 10, 19, 20, 41, 65} Corrosion of copper alloys by sea water is much more complicated in its factors and more pronounced than true of fresh waters, a fact related to the much greater activity of sea water on copper itself.

Average corrosion rates of the alloys in quiet exposure or in moderate flow are on the order of 1 to 10 mg. per sq. dm. per day. Strong aeration and particularly rapid flow push average rates up to 20 to 60 mg. per sq. dm. per day for the high copper bronzes, the range for the aluminum bronzes and brasses being somewhat less than this.

These rates as noted are average over-all rates. Exposure of the copper alloys to sea water, however, leads often to localized action—pits, grooves, and in the case of the high brasses, dezincification. Thus in ten-year tests reported by Bassett and Davis,⁶ in which tubes of different alloys were exposed to sea water in horizontal gravity flow through them, localized attack was characteristic. Whereas over-all corrosion rates ran around 1 to 2 mg. per sq. dm. per day, localized attack took place in the worst cases at rates of 250 to 300 mg. per sq. dm. per day. Brasses with 20 to 30% zinc behaved excellently, rates of localized attack keeping below 20 mg. per sq. dm. per day, without dezincification. An alloy with 10% zinc was equally good, but localized attack of 15 and 17% zinc alloys ran as high as 100 to 150 mg. per sq. dm. per day. High zinc brasses were badly dezincified with the exception that 63 Cu 36 Zn 0.5 Sn was unusually good, with localized attack of less than 2 mg. per sq. dm. per day. Tin bronze was reasonably good, with a maximum rate of 20 mg. per sq. dm. per day; and aluminum bronze was poor with localized rates of 15 to 60 mg. per sq. dm. per day.

In conjunction with these results it is interesting to consider the data obtained in tests where specimen bars were exposed to Bristol (England)

Channel water for four years. Their location was such that they were submerged 93% of the time.²¹ The results are given in Table 310.

TABLE 310.— *Copper Alloys vs. Sea Water.*

	Ave. corrosion rate — mg. per sq. dm. per day	Remarks
70 Cu 28 Zn 2 Pb	22	No dezincification
62 Cu 37 Zn 1 Sn	24	Some spotty dezincification
61 Cu 39 Zn	12	Some spotty dezincification
60 Cu 39 Zn 1.3 Pb	6	No dezincification

No pitting or localized attack other than the spotty dezincification mentioned was noted.

The ten-year test results described on page 448 are extremely interesting for a number of reasons, but especially in illustrating so forcibly the extreme variability in behavior of the copper alloys, as a group and individually, to flowing sea water. A single specimen may have a high general resistance and still in a localized spot or two be very rapidly attacked. Copper alloys, corroding even slightly in sea water develop at their surfaces liquid and solid films of corrosion product that have a potentially suppressive effect on further corrosion. Yet the movement of sea water particularly when carrying entrained air bubbles and when turbulent often upsets the full protective effect of these films. Where locally upset, local action takes place with a speed that is determined by the power and persistence of the concentration cells that result.

The building up and break-down of these films depend on an extremely complex group of factors, both chemical and physical, relating to the compounds formed and their physical characteristics, and to the forces of motion and impingement of the water. A further complicating factor is the formation of deposits from the water itself.

The fact that sea water is an excellent conductor makes possible the very rapid corrosion rates sometimes observed in sea water, by intensifying the power of the cells.

One of the more difficult of sea water conditions to handle is that of condenser tubes, particularly on board ship. In this service 70 Cu 30 Zn and 70 Cu 29 Zn 1 Sn are most generally used and are widely successful. Their ultimate life is determined by slow dezincification in the less stringent exposures, tubes lasting 10 to 20 years (about 20 to 40 mg. per sq. dm. per day). Rarely, in more destructive exposures, localized attack may run as high as 400 mg. per sq. dm. per day (one year life) and higher. The 60 Cu 40 Zn tube, commonly used for fresh water conditions, has little utility for sea water, invariably suffering rapid dezincification. Copper and the tin bronzes are much more susceptible than the brasses to localized as well as general attack, under condenser conditions. A relatively recent alloy that has par-

ticular virtue is 76 Cu 22 Zn 2 Al. This has handled, reasonably well to excellently, conditions under which brass itself has been unsatisfactory. Aluminum bronze is little used, due to high cost, but at times has given good results.

Bengough and May¹⁰ have classified the types and characteristics of scales that appear on brass condenser tubes. (See Table 311.)

TABLE 311.—*Types of Scales on Brass Tubes.*

Type	General Property	State of Aggregation	Principle Visible Constituents
1	Usually highly protective	Usually very finely crystalline	Calcium carbonate; ferric compounds
2	Highly protective	Vitreous in lower layers	Difficult to identify. Probably largely zinc hydroxide and cupric hydroxide; possibly also calcium sulfate
3	Highly protective where vitreous. Much less protective where crystalline	Vitreous and crystalline; proportions vary from mainly vitreous to mainly crystalline	Copper crystals; zinc hydroxide and oxychloride. Sometimes traces of copper compounds
4	Only slightly protective (underlying tubes specially liable to pitting)	Mainly crystalline. Vitreous in patches	Cuprous oxide, sometimes small copper crystals, cupric hydroxide, cupric oxychloride, some calcium sulfate, "zinc oxychloride"
5	Fairly protective (underlying tubes specially liable to fail by scale erosion)	Mainly crystalline; not very adherent	Cupric hydroxide, basic carbonate, cupric oxychloride, "zinc oxychloride," calcium sulfate

The reader is referred to the original paper for an extremely interesting and instructive study of scales.

Recently a number of investigators have tested the resistance of condenser tube alloys to jet-impingement conditions.^{10, 12, 19, 20, 41, 44} Some very rapid rates of attack have been obtained. In one set of tests⁹ a water stream flowing at a velocity of 10 ft. per sec. was made to impinge at a right angle on specimens of 70 Cu 30 Zn, the temperature being 68° F., the time 28 days. Increasing the entangled air content of the water stream increased attack very greatly. (See Table 312.)

TABLE 312.—*Brass vs. Chloride Solution.*

Entangled air cu. cm per hr.	Penetration inches	Calculated corrosion rate Mg. per sq dm. per day
0.7	<.0004	<29
25	<.0004	<29
145	<.0004	<29
3,000	.015	1100
11,000	.040	2900

The importance of air bubbles as a factor is well illustrated. The highest rate given is not greater than those that have been rarely observed in actual tube installations.

In the present state of understanding of the sea-water, condenser-tube corrosion problem, it may confidently be stated that turbulent flow of cooling water carrying entrained air bubbles is the first necessary condition favoring rapid corrosion, but this condition may or may not lead to rapid corrosion, and that in general aluminum brass (76 Cu 22 Zn 2 Al) in service has given in more cases than not a better account of itself than Admiralty brass and 70 Cu 30 Zn.. On the other hand, it still is not possible to predict what behavior a tube material is going to give, under average to severe condenser conditions, and furthermore fool-proof practical means of preventing rapid attack on the brasses have not yet evolved.

ATMOSPHERE

In atmospheres^{18, 27, 28, 29, 60, 61, 62, 63, 64} the bronzes behave much like copper, the brasses in a somewhat inferior manner. In rural atmospheres rates range well below 1 mg. per sq. dm. per day, in urban atmospheres about 1 to 2 mg. per sq. dm. per day and in marine atmospheres around 1 mg. per sq. dm. per day.²⁸ In heavy sulfurous atmospheres rates climb much higher, e.g. around 40 to 60 mg. per sq. dm. per day in the smoke jack of a railroad roundhouse.^{63, 64}

The bronzes tarnish in atmospheric exposure to a dull, sometimes black finish, the tarnishing being more pronounced and rapid in sulfur-bearing industrial atmospheres. Green salts may develop under some conditions. The brasses of higher copper content tarnish more rapidly than the high zinc brasses, the latter tending to dull rather than tarnish in the early stages. For indoor and outdoor architectural purposes where various shades of yellow and red-yellow of the brasses and the appearance of nickel-silver have esthetic interest, tarnishing may be prevented by periodical cleaning or by the application of lacquers. Tarnishing of brasses has been given a good deal of study by Vernon.⁶⁰

An extremely good illustration of behavior is afforded by the tests of Hudson,²⁹ in which hard-drawn wire (.066 in dia.) and strip (.02 in. thick)

were exposed two years on the roof of a building in South Kensington, London. From the loss in tensile strength the equivalent average thickness (in. per yr.) of the corroded layer was calculated. (See Table 313.)

TABLE 313.—*Copper Metals vs. Outdoor Urban Atmosphere.*

	In. per year	Mg. per sq. dm. per day
Copper000186-266	1.15-1.65
99.05 Cu .91 Sn000245	1.52
98.72 Cu .67 Zn000195	1.21
99.16 Cu .76 Si000213	1.32
98.94 Cu .96 Cd000215	1.33
70.83 Cu 29.14 Zn000637	3.8
70.29 Cu 29.66 Zn001321	7.8

Hudson attributed the greater damage to the brasses to dezincification. In an earlier paper²⁸ he refers further to evidences of dezincification in outdoor exposure.

Typical examples of atmospheric uses of bronze are trolley, cable and power transmission wires, catenary bolts and fittings. Silicon-manganese bronze and phosphor bronze are common materials for parts not carrying current, and copper alloyed with low content of silicon, tin, cadmium, etc., for conducting parts. Brasses are widely used for bolts and similar accessories.

HIGH TEMPERATURES

The copper alloys are widely used in the elevated temperature range up to 700° to 800° F. Above this range both progressive oxidation and lack of strength are limitations. There is widespread use of aluminum bronze exhaust valve seats in aircraft engines, a service involving temperatures around 750° F. According to Bassett,⁵ aluminum bronzes are used a good deal at elevated temperatures because of good scaling resistance. He states further that many of the alloys of copper scale at red heat and above red heat, and that brass gradually loses zinc by volatilization above 840° F.

With respect to brass, Dunn¹⁷ has concluded as follows:

"The zinc-copper alloys fall, as far as their behavior under oxidation is concerned, into two classes, fairly sharply separated. Those with copper contents below about 80% all oxidize at essentially the same rate, and all give rise to an oxide which is almost pure zinc oxide. Those with copper above about 86% oxidize at approximately the same rate as copper, and the oxide contains the metal in the same proportion as the original metal. The first or zinc-forming class oxidize at about one-eighth of the rate of the second or copper oxide-forming class.

"The rate of oxidation increases exponentially with temperature, doubling itself approximately for every 75° C. rise in temperature."

He found also that aluminum had a very beneficial effect, an alloy with 1.9% aluminum having a low rate of attack up to 1472° F.

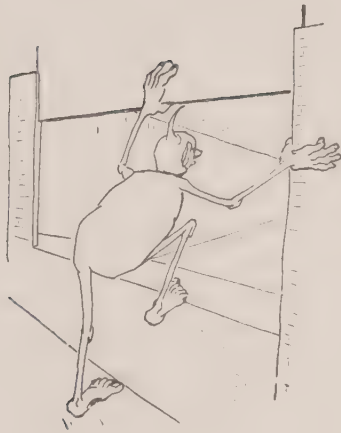
COPPER ALLOYS

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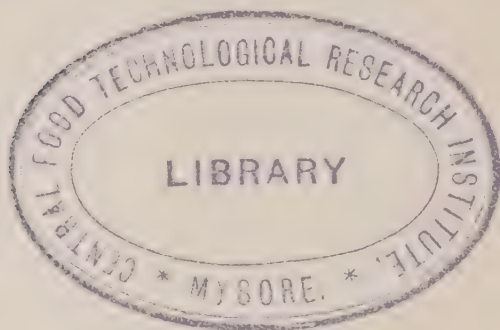
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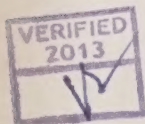
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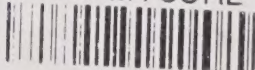
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